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Towards suitable tests for the migration of metals from ceramic and crystal tableware

Work in support of the revision of the Ceramic Directive 84/500/EEC

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Abstract

Food Contact Materials (FCMs) are regulated in the European Union to ensure the functioning of the internal market and protect the health and interests of the consumers. For ceramics, limits exist only for lead and cadmium under Directive 84/500/EEC but scientific data has shown the need to lower these and to consider limits for other metals. In addition, no harmonised European legislation exists for the glass sector.

In initial consultation with Member States, the Commission defined so-called discussion starting values ('DSV') for potential future limits based on an initial risk management discussion. These DSV's were used to verify to what extent the analytical method would give a realistic estimate of the actual migration of metals to the food, and whether suitable analytical methods would be available. Both Member States and stakeholders identified too limited scientific knowledge on the migration of these metals into food and its testing.

The Commission's Directorate-General Health and Food Safety (SANTE) thus entrusted the European Commission (EC) Joint Research Centre (JRC) to investigate testing methods for migration of metals from ceramics and glass. Between 2013 and 2017 the JRC's European Reference Laboratory for FCMs (EURL-FCM) generated over 6000 data points on hundreds of samples provided by industry. The findings of a series of studies on suitable test methodologies for tableware and cookware are summarised in this synthetic final report.

For ceramics, the repeated use of tableware should be simulated by three successive migration tests, as the first test only gives an unrealistically high estimate of the migration after a few uses. The repeat test of three successive migrations for 24 h at 22 °C using acetic acid 4% to simulate the worst (acidic) foods is appropriate. A lapse of time between migration tests (owing to a week-end) has little effect, thus allowing to start tests any day for a better productivity.

Storage of articles has a limited effect on the migration of metals for ceramics. Thus tableware used occasionally is covered fairly adequately by a repeat test. Testing the migration from rim of decorated hollowware can be adequately done using existing ISO/CEN standards. Although the data set for bakeware is limited, early results indicate that the same test could be used.

For crystal, the test conditions must reflect the conditions of use. A repeat test with acetic acid 4% of 2 h at 22 °C is an adequate reflection of exposure and allows completing the repeat testing for compliance in one working day. A long storage leads to a re-increase in the value of the migration. Consequently a limit value on the first migration of the repeat test may also be indicated. The specific establishment of a limit value for crystal may necessitate a review of exposure assessment.

Several analytical methods can be used with satisfactory performance to analyse the resulting migration solutions at the level of the DSVs for lead, cadmium and other metals. The performance of the official control laboratories was also satisfactory for enforcement at these levels, as shown by two interlaboratory comparisons.

1 Introduction

Food Contact Materials (FCMs) are regulated in the European Union under a food safety umbrella to ensure the functioning of the internal market and protect health and interests of the consumers.

The migration of lead and cadmium from ceramic into food is presently regulated under Council Directive 84/500/EEC[1]. It defines a maximum migration of 4 mg/kg food for lead and 0.3 mg/kg food for cadmium. Limits have not been updated since. Scientific data has shown the need to lower these and to consider limits for other metals as well.

In opinions published between 2009 and 2012 the European Food Safety Authority (EFSA) identified the high exposure of consumers to lead and cadmium from food related sources[2],[3]. EFSA concluded that lead may cause adverse effects in children at levels as low as 30 µg/day, adults would be affected at slightly higher levels. Present exposure from all sources is above these limits. Therefore exposure from FCMs should be reduced to values well below these limits, since the limits in other sectors have already been much decreased. For example a 10 µg/kg food limit is set for drinking water in the Drinking water Directive[4]. For metals and alloys used in food contact applications, a guidance from the Council of Europe[5] also recommended low levels expressed as Specific Release Limits (SRLs) for a number of metals. The use of lead and cadmium is also severely restricted under the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH).

From a technical standpoint, the European Ceramic industry produces mostly in a traditional/artisanal manner from which it gathers its appeal. Such production techniques may rely on the intentional use of lead, cadmium and other heavy metals, and cannot readily be changed without changing the traditional/artisanal ways of production. Most mainstream ceramic materials already meet low values of migration, in particular for lead, but traditionally produced ceramic articles do not. Some articles on the market migration near the present limit of 4 mg/kg food. Crystalware has been not covered by a harmonised legislation to date. Setting limits for metals requires an understanding of the migration both in acidic drinks such as wine and on the feasibility of developing test methods representative of such migration.

Several Member States including Germany asked the Commission to lower the limits for the migration of these heavy metals from ceramic FCMs, in order to maintain a high level of consumer protection. Member States and stakeholders would also favour a harmonised legislation for the glass/crystal sector.

Several consultations and meetings, involving both Member States and industry highlighted the challenges of lowering the limits - for both scientific as well as economic reasons. DG SANTE asked the JRC to undertake a research project of supporting data on testing methods and migration behaviour to ensure the enforceability of future measures and aid the decision-making process for the EC, Member States and stakeholders.

[1] Council Directive 84/500/EEC of 15 Oct. 1984 on the approximation of the laws of the Member States relating to ceramic articles intended to come into contact with foodstuffs

[2] European Food Safety Agency, Scientific Opinion on Lead in Food, EFSA Journal (2010); 8(4):1570; 1-151

[3] European Food Safety Agency, Scientific Opinion. Cadmium in Food, EFSA Journal (2009): 980; 1-139

[4] Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption, OJ L 330, 5.12.1998, p. 32–54

[5] Council of Europe, Metal and alloys used in food contact materials and articles. A practical guide for manufacturers and regulators, the Committee of Experts on Packaging Materials for food and Pharmaceutical Products (P-SC-EMB), 1st Edition, 1-216, (2013)

2 Approach and considerations used in the study

2.1 Scope

The scope of the study was to investigate the feasibility of the current analytical methods to quantify a range of metals at low levels upon migration from tableware. It also included a comparative experimental investigation of conventional migration tests and their comparisons to real life worst case migration in food. It considered testing for multiple use (of service-life) as well as occasional use of some tableware articles. It also took into account the feasibility and practical aspects of testing, as well as testing different types of tableware/drinkware/bakeware, different materials (ceramics, terracotta, crystal etc.). It also included reliability of results across laboratories for enforceability.

Note: The study did not cover aspects of exposure which are part of the EFSA mandate. However, kinetics and data generated in food simulants and foods could be of use for exposure assessments. The study also did not cover any setting of numerical values for limits. The targets taken for the work on technical feasibility of tests used ranges of values discussed at Commission and Council of Europe level. The range on metals analysed was as broad as the techniques allowed, but did not imply an intention for regulatory purposes.

2.2 Objectives

Some key research questions included:

Can an adequate migration test be developed to be conservative for safety but comparable and reflecting the service life for multiple uses of tableware and cookware?

Can testing be also developed to reflect migration from drinkware and the glass sector, and can testing cover a service life regardless of the frequency of use of these articles?

Can current analytical methods be amenable to quantify lower levels for lead and cadmium but also other metals in simulant solutions? Can they demonstrate adequate performance for official controls and compliance testing?

2.3 Collaboration

The project included a stakeholder platform. The expert group was an open group where all were informed and could also participate in regular meetings. Six workshops were organised over the span of the work from February 2013 to October 2016[6]. They served to brief stakeholders and experts on the results generated by the JRC, or done in tandem between laboratories. They also served to exchange information for the further work planning. The summaries of the meetings were circulated.

The participatory approach was very important to build trust and to provide a flexible work plan which could evolve as a function of the sets of results obtained. It also anchored collaborations with the professional associations for the supply of test samples (articles). More than 4500 test pieces representing more than 100 types of articles were donated by the industries and professional associations towards the project to be used as test samples, both in research studies and towards interlaboratory comparisons testing.

2.4 Articles used as test samples

Both commercially available and ad-hoc produced articles (used as test samples) were selected on the basis of an expected significant migration of metals (as non-releasing samples were not suitable for method development[7]). The collection of commercial articles aimed to represent the diversity of the market as best as possible (Figure 1), including in type of manufacturing (broadly understood are more industrial vs. more

[6] 21/02/2013 workshop 1; 24/10/2013 workshop 2; 10/04/2014 workshop 3; 10/12/2014 workshop 4; 12/10/2015 workshop 5; 25/10/2016 workshop 6

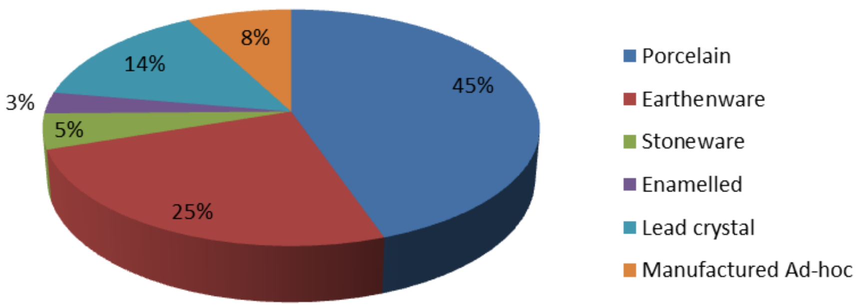
[7] The samples thus do not represent a realistic representation of the market-by-market share.

artisanal-traditional), colours, glazing, types of metal, nature of articles (ceramics porcelain, terracotta, decorated glass, crystal, enamel etc.), and type of articles (tableware, drinkware, cookware).

In the call for samples, the European association Ceram-Unie as well as the Italian association Cofindustria provided a link to individual producers. In order to avoid bias and protect proprietary information, the study did not ask for specific compositions of the articles donated for the project. The articles were also treated anonymously in the reports. Stakeholders who donated samples received their own raw data.

Some articles were produced ad-hoc to generate a migration of metals in the range of values around the intended limits at lower concentration levels. They also aimed to be as homogenous as possible to minimise variations between test specimens of the same batch and thus highlight the differences between results obtained from different migration protocols when they were compared. Three different categories were studied: flatware (first category[8]), hollowware (second category) and cookware (third category). Crystalware articles were also investigated. The description of the tests samples and panorama of tests performed are reported in Annex 1.

Figure 1: distribution of samples (n= 103) obtained for the studies



2.5 Targets for analytical values

Council Directive 84/500/EEC establishes specific migration limits (Table 1) and basic rules for determining the migration of lead and cadmium in ceramics. It also reports test conditions to carry out the migration test using acetic acid 4 % and an exposure contact time of 24 ± 0.5 h at 22 ± 2°C.

Table 1: Current limits for lead and cadmium (Directive 84/500/EEC) and DSVs

Category	Current limits		DSV	
	Lead (Pb)	Cadmium (Cd)	Lead (Pb)	Cadmium (Cd)
1ª	0.8 mg/dm²	0.07 mg/dm²	2.0 µg/ dm²**	1.0 µg/dm²**
2ª	4.0 mg/L	0.3 mg/L	**10 µg/kg**	**5 µg/kg**
3ª	1.5 mg/L	0.1 mg/L	3.8 µg/kg**	1.9 µg/kg**

1ª Articles that cannot be filled and articles that can be filled; the internal depth does not exceed 25 mm; 2ª Articles that can be filled; 3ª Cooking ware; packaging and storage vessels having a capacity of > 3L. ** calculated related to the 2ª category

As the JRC required target values to investigate the performance of quantification at lower levels, DG SANTE proposed numerical values to take into account the revised EFSA opinions for a number of elements. These were called discussion starting values (DSVs) which were based on an initial risk management discussion. These DSV's were used to verify to what extent the analytical method would give a realistic estimate of the actual migration of metals to the food, and whether suitable analytical methods would be available. The limits for lead and cadmium in drinking water under the Drinking Water

[8] in the ceramics Directive

Directive were chosen as DSV for ceramic FCMs. The DSVs would reduce the migration by a factor 400 from 4 mg/kg food to 10 µg/kg food for lead, and by a factor of 60 from 0.3 mg/kg to 5 µg/kg food for cadmium. Metals other than lead and cadmium are not yet regulated at European level, but limits for some metals are under discussion. The DSVs for several additional metals that could be present in ceramic samples are listed in Table 2 in comparison to SRLs used by the Council of Europe for metals and alloys.

Table 2: DSVs and SRLs in µg/kg for elements other than lead and cadmium

Metal	Abbrev.	DSV	SRL	Metal	Abbrev.	DSV	SRL
Selenium	Sn	50000	100000	Manganese	Mn	400	1800
Iron	Fe	2500	40000	Chromium (soluble)	Cr	100	250
Zinc	Zn	1500	5000	Cobalt	Co	84	20
Vanadium	V	1200	10	Nickel	Ni	72	140
Aluminium	Al	1000	5000	Silver	Ag	50	80
Barium	Ba	1000	1200	Antimony	Sb	40	40
Copper	Cu	1000	4000	Arsenic	As	18	2
Lithium	Li	600	48				

2.6 Experimental designs

2.6.1 Test protocols

2.6.1.1 Food and food simulants

Two test protocols for the migration of metals from ceramic in simulants (liquid simulating foods) were compared to a protocol mimicking exposure to a food of acidic nature which represented a "wort case" scenario (a food is considered acidic when its pH is below 4.6).

Tomato was proposed as benchmark of both a common and a worst case food for ceramic articles. Food composition tables[9] report a range of pH for tomato sauce/paste from 3.5 to 4.7. A study was conducted on about 40 brands of tomato products to test the range of acidity, which did not indicate an acidity lower than pH 4.2. A follow-up study was thus done to compare the result of a migration test from ceramics into tomato of commercial pH (4.2) and into a tomato paste acidified to pH 3.5.

In the case of crystal, the worst case beverage chosen was an acidic wine with a pH of 3.2. A white wine was chosen to avoid interference of the matrix during the analysis.

2.6.1.2 Identification of a test method for ceramics

European Directive 84/500/EEC stipulates a conventional test using 4 % acetic acid solution as the simulant for ceramics and 24 h at 22 °C as time-temperature exposure. This test is also an ISO standard and a national standard in a large number of countries. In this test, the value of the first migration is taken. Yet, if the limit is based on actual exposure rather than on a conventional migration test, a test that more realistically represents actual use is required. Given that many ceramic materials show a much higher migration during the first use than during subsequent uses, a repeated use test of three subsequent migrations represents better the exposure after the first use of a ceramic material[10]. This protocol was therefore investigated to generate results for three successive migration tests in order to represent a repeated use regime.

Unless intended for cooking, the worst condition of use of ceramic articles is hot-fill. Under this condition the article is filled with a hot food, and then left to cool down before

[9] US FDA/CFSAN - Approximate pH of Foods and Food Products.
[10] note: the same approach is also used for plastic materials intended for repeat-use

the food is consumed. Generally a testing condition of 2h at 70 °C is considered to represent conservatively this use. However, for practical reasons including safety issues of laboratory operations handling hot acetic acid (corrosive fumes) and difficulties in constant temperature control during migration testing, a condition at room temperature has historically been preferred for ceramic materials.

As the duration of a repeat test becomes 3 days, options to potentially accelerate a repeat-use testing were considered for comparisons. An increase of temperature to reduce the time of exposure, while feasible, would cause implementation issues for acetic acid (fumes). Alternative conditions were considered such as the one used by the Council of Europe for metals and alloys with 0.5 % citric acid for 2 h at 70 °C. The introduction of an accelerating pre-conditioning step of higher acidity (10 %, 5 h at 22 °C) was also attempted followed by one single migration with acetic acid 4 % (24 h, 22 °C).

Literature suggested that leaving decorated (overglaze) ceramic articles (i.e. overnight or week-end) between repeat tests may cause higher migration of lead. Multiple migrations with a so-called "weekend gap" of 72 h between migration tests were investigated to evaluate its effect on the result of a compliance test.

The scope of the study encompassed both daily use ceramic articles as well as several luxury porcelain items of which the expected use could be occasional. In this context, a study was done on the effect of storage on the migration of metals. Articles were tested for migration, stored for different periods from one week to six months, and re-tested to assess the possible evolution of the migration of metals.

Methods to test migration specific to the rim were also investigated to compare two standards (ISO/CEN and ASTM) that are commonly used but not required in the current legislation. The aim was to compare the two protocols of the standards.

Testing conditions for cookware were investigated. Kinetic studies into tomato sauce were performed in boiling tomato sauce (pH 3.5) up to 6 h and analysing the migration of lead at several time points. Repeated use tests under different conditions in both simulants and food were compared.

The overall experimental plan is summarised in Table 3.

Table 3: Overview of experimental design for ceramics

Aim of work	Tests done
Optimisation of the migration test	- 3 tests in acetic acid 4 % (24 h at 22 °C) - 3 tests in citric acid 0.5 % (2 h at 70 °C) - 3 migration tests in tomato sauce (regular/acidified), (2 h at 70 °C) - Conditioning in acetic acid 10 % (5 h at 22 °C) then test in acetic acid 4 % (24 h at 22 °C)
Effects of gap between test	- Testing with 72 h (week-end) between 1st and 2nd migration tests - Testing with 72 h (week-end) gap between 2nd and 3rd migration tests
Storage effect	Repeat testing of the same ceramic articles - after six months, one month, one week of storage (3 migration tests) - 3 migration tests with acetic acid 4 % (24 h at 22 °C)
Study on cookware	- 3 consecutive migration tests with acetic acid 4 % (24 h at 22 °C) - 3 consecutive kinetics with boiling tomato sauce (pH 3.5) for 6 h

2.6.1.3 Identification of a test method for crystalware

Investigations on the migration of metals from crystalware into the representative worst case food and into simulants were conducted. This included tests on "repeated use" by conducting experiments testing successive migrations. Kinetics of migration were also investigated both in wine and in the 4 % acetic acid conventional simulant to assess test conditions (0.5 h, 1 h, 2 h, 24 h and kinetics of 24 h), and in three successive migrations. In addition, an alternative testing was attempted using a "pre-conditioning" of the test samples with acetic acid 10 % during 5 h followed by a single migration of 24h with acetic acid 4 %. A third approach was also explored using 0.5 % citric acid for 2 h at 70 °C to maintain the comparisons similar to that of performed for the ceramics articles.

The overall experimental plan is summarised in Table 4.

Table 4: Overview of experimental design for crystalware

Aim of work	Tests done
Optimisation of the migration test	- 3 tests in acetic acid 4 % (24 h at 22 °C) - 3 tests in citric acid 0.5 % (2 h at 70 °C) - 3 tests in wine (24 h at 22 °C); - 3 tests in wine (4 h at 22 °C) - 3 short time tests in acetic acid 4 % (0.5 h at 22 °C) - 3 short time tests in acetic acid 4 % (1 h at 22 °C) - 3 short time tests in acetic acid 4 % (2 h at 22 °C) - Conditioning in acetic acid 10 % (5 h at 22 °C) then test in acetic acid 4 % (24 h at 22 °C)
Storage effect: Repeat testing of the same crystal articles	Occasional use - after 18 or 13 or 11 months of storage (3 migration tests in acetic acid 4 %, 24 h at 22 °C) - after one month of storage (3 migration tests in acetic acid 4 %, 24 h at 22 °C) - after one week of storage (3 migration tests in acetic acid 4 %, 24 h at 22 °C) Daily use: - 3 migration tests wine (1 h at 22 °C, over 7 days)
Kinetics of migration	- 3 consecutive kinetics in acetic acid 4 % over 24 h at 22 °C (10 time points) - 3 consecutive kinetics in wine for 24 h at 22 °C (10 time points)

2.6.1.4 Migration

For each test protocol, 4 identical samples (articles) were taken, cleaned with non-acidic diluted detergent at 40 °C, rinsed with purified water and dried. The samples were filled with the simulant to a level of 1 mm from the brim. The migration test was carried out in the dark in an incubator to maintain the temperature controlled. In repeat-use testing, the samples were exposed to the simulant three times. After the first migration (I), the samples were rinsed and dried. They were refilled with fresh simulant and incubated for the second migration (II). The same procedure was followed for the third migration (III). The lapse of time was less than 1 h between migrations.

2.6.1.5 Sample treatment after migration and analysis.

Migration solutions were treated in the same manner before the instrumental analysis, as described in the individual reports. This included the addition of internal standards which were chosen following a discussion with experts and in-house research. These were diluted to the calibration range corresponding to the expected migration of metals. The samples treatment for the tomato paste included a digestion using microwave.

2.6.2 Analytical quantification at low levels

The measurement of the migration of metals from articles into liquids simulating foods has three sources of uncertainty in the results. One comes from the migration test itself. The second comes from the analytical quantification of the levels of the metals themselves in the matrix (liquid) in which they have migrated, and the third from the entire procedure, also including lag times and sampling[11].

[11] A fourth source of variability in the results can be the apparent inherent variability in ceramic samples which is not related to the analytical work but rather to the production of ceramic materials.

Two interlaboratory comparisons (ILCs) were organised to assess the performance of laboratories via the so-called accuracy[12] and precision[13] for:

— The quantification of metals in acetic acid migration solutions at the level of interest close to DSVs, and including a variety of metals (Ba, Co, Mn, Pb, Cd, Ni, As, Al)

— The two protocols of the migration step followed by the quantification from two types of articles (decorated glass and ceramics).

As several instruments can be used to measure metals in solutions, the ILCs were done for different analytical techniques that are most used, namely inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES) and graphite atomic absorption spectrometry (GF-AAS).

2.7 Survey on frequency of use of tableware

The JRC conducted a survey to understand what was perceived as occasional use for consumers for different types of tableware, crystalware and cookware. An on-line survey was launched during a JRC open-day. In total, 596 surveys were collected. Although 81 % of respondents were of Italian nationality, a number of other nationalities were also represented in smaller percentages (Belgian, French, Netherlands, Bulgaria, Denmark, Estonia, Finland, Greece, Hungary, Lithuania, Poland, Portugal, Romania, Spain, Sweden and United Kingdom). The ratio of gender of respondents was of 67 % female and 33 % male. The age range was for 30 % of respondents below 18 years old, for 50 % in the 19-50 age range, and for 20 % beyond 50 years old. The occupation statistics showed about 35 % students, 50 % employed, and 15 % at home or other.

[12] Closeness of a measured value to a standard or known value.
[13] Closeness of two or more measurements to each other.

3 Results

All results reported were average values and the corresponding standard deviation was derived from four replicates obtained at the first (I), second (II) and third (III) migration. The results for flatware (Cat. 1[a]) were expressed in µg/dm^2, and for hollowware (Cat. 2[a]) and cooking ware (Cat. 3[a]) in µg/kg (Annex 2). A number of samples were analysed by three National Reference Laboratories (NRLs) on a voluntary basis.

3.1 Identification of suitable migration test

The original focus was mostly on lead and cadmium since those are primarily affected for the revision of the Directive EC 84/500/EEC. The scope was then extended to cover more metals to provide a better overview. Together with the lower intended limits, the development of tests focused on including repeat-use (i.e. 3 migration tests for enforcement/compliance) into migration simulant solutions. As previously stated, it included a comparative experimental investigation of conventional migration tests and their comparisons to real life worst case migration in food. It considered testing for multiple use (of service-life) as well as occasional use of some tableware articles. It also took into account the feasibility and practical aspects of testing, as well as testing different types of tableware/drinkware/bakeware, different materials (ceramics, terracotta, crystal etc.). The project included duplicate experiments with the volunteer cooperation from the NRLs of Belgium, Germany and the United Kingdom[14] in order to generate more data. It also included reliability of results across laboratories for enforceability.

3.1.1 Migration testing from ceramic tableware

The migration of metals from 81 ceramic samples and two reference materials was investigated under different conditions. It considered food and simulants, test time-temperature conditions, and repeat-use tests to simulate long shelf life.

It covered different types of ceramic articles including tableware and bakeware, and was comprehensive of all metals that can migrate. The sets of samples studied aimed to represent a vast variety of articles including hand crafted and highly decorated samples more prone to migration a broader range of metals and at greater levels.

Some definitions in the sector of ceramic tableware

— Ceramics are either vitrified or semi-vitrified as is the case with earthenware, stoneware, and porcelain.

— Earthenware is glazed or unglazed nonvitreous pottery which has normally been fired below 1200 °C. Due to its porosity, earthenware, with water absorption of 5-8 %, must be glazed to be watertight.

— Terracotta is a type of earthenware, it is a clay-based unglazed or glazed ceramic, where the fired body is porous. The term is also used to refer to the natural, brownish orange colour.

— Stoneware is fired at a relatively high temperature (typically between 1180 °C to 1280 °C). It is a vitreous or semi-vitreous ceramic made primarily from stoneware clay or non-refractory fire clay. It is nonporous and it may or may not be glazed.

— Porcelain, bone china and stoneware, all fired at high enough temperatures to vitrify, temperatures between 1,200 and 1,400 °C. Strengths, and translucence of porcelain, arise mainly from vitrification.

The study also included a few (three) enamelled articles. They were considered together with ceramics due to the limited size of sample set available (descriptions in Annex 1).

3.1.1.1 General considerations

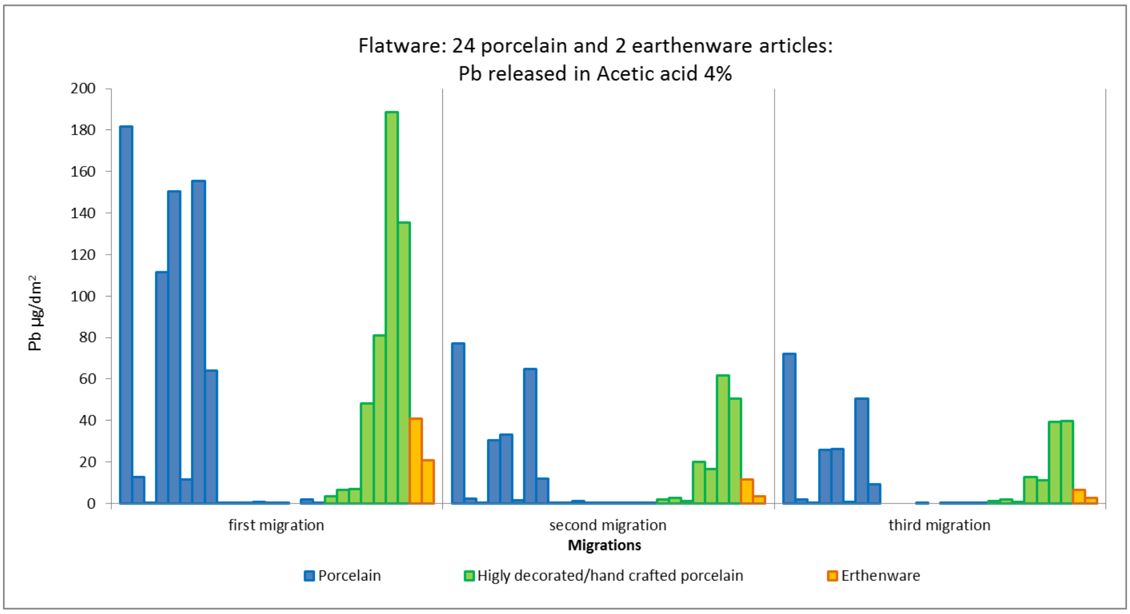
In the sets of samples investigated, a number of metals were found in migration solutions e.g. aluminium (Al), iron (Fe), zinc (Zn), cobalt (Co), lithium (Li), barium (Ba),

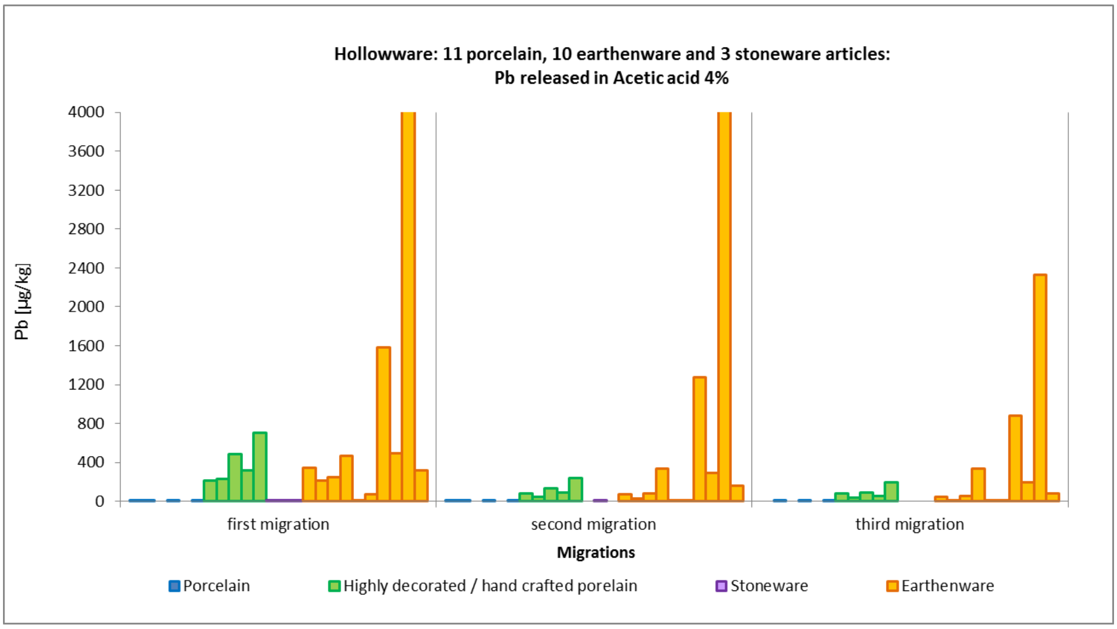
[14] NRL-BE: Scientific Institute of Public Health (ISP); NRL-UK: FERA Science LTD; and NRL-DE: Federal Institute for risk assessment (BfR)

manganese (Mn), vanadium (V), lead (Pb), cadmium (Cd), antimony (Sb), titanium (Ti), chromium (Cr), nickel (Ni), copper (Cu) and arsenic (As). For enamelled articles the migration of lead and cadmium was low while other metals could be detected such as aluminium, manganese, iron, cobalt, zinc, copper, barium, lithium and titanium.

The migration was higher for the more "artisanally" produced articles that are often unique/ specialty items (Figure 2). This highlights a "sensitive" nature of articles like earthenware or porcelain that could not pass a low DSV level, especially for lead.

Figure 2: Values of the 1st/2nd/3rd migration for flatware and hollowware for "sensitive" products





Yet, it should be noted that the effects of a more severe conventional test can lead to physical damages that would not otherwise occur in normal use in the home even over years of service life. Damage such as discolouration, attack, formation of salt crystals or leaks from porous articles during test is illustrated in Figure 3.

Figure 3: Some effects of acetic acid 4 % test on ceramic samples (earthenware)

The blue and red plates for example were purchased for home use, with an additional set for testing. The testing had an immediate effect on the two types of plates. Being earthenware, it was clearly seen that the simulant attacked the porosity. These articles exceeded the intended new limits at the third migration test for lead and cadmium. Yet those plates did not exhibit damage when used daily for over four years.

3.1.1.2 Benchmarking with food vs. simulants

A model of food served as reference for worst case exposure. This food had to be a common one, yet it had to be a fairly worst case of acidity since acidic foods are the ones tending to extract the most metals from materials such as ceramics or crystal.

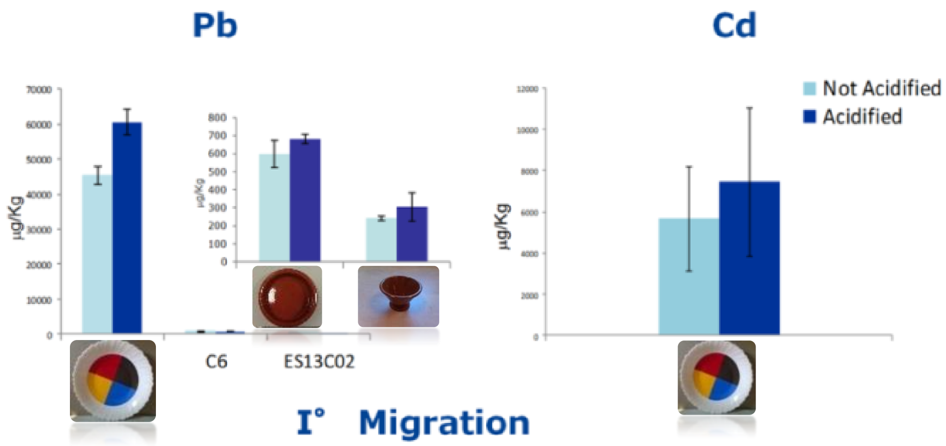
For ceramics, this food was chosen as a tomato puree/paste-concentrate. This choice to a tomato paste considered that although some berries tend to be the most acidic foods, they are not often consumed in an acidic peeled form. Similarly, lemon is not commonly consumed as hot food.

A number of formats were tested to select a consistent source for the duration of the project. The tomato type selected was a double concentrate (28 % min) of large cans (2.5 kg). The concentrate offered a larger amount per batch after dilution and was an advantage for shipping to NRLs doing analyses. The large cans ensured a good consistency in composition and little effect from the packaging (larger volume of food with respect to the surface of the container). It had no fat content to avoid complicating the analytical work. The pH was also around 4.2 like all other commercial tomato products tested rather than the worst theoretical pH of 3.5.

This worst case food was also made to be the worst of its theoretical acidity rather than its commercial (edible) counterpart. A study comparing repeat migration tests from ceramics into tomato sauce of commercial pH (4.2) and that of acidified sauce to pH 3.5 under conditions of hot fill (2 h at 70°C) was conducted. The results from the first migration were sufficient to identify that the level of acidity induced a difference in migration (Figure 4). The difference was not as extensive as would have been expected. Since it could not be demonstrated that a tomato sauce could never be of pH 3.5, it was decided to take the pH 3.5 as reference for worst case and to acidy all batches of tomato. A significant amount of acid[15] was necessary due to a buffering effect of the tomato proteins and carbohydrates.

[15] A solution of 120 g citric acid at 20% (w/v, pH 1.56) was needed to acidify 670 g of tomato then diluted 1:3.

Figure 4: Migration of lead and cadmium into acidififed vs. non acidified tomato sauce



As a consequence, it should be kept in mind that when a comparison was made with the worst foreseeable food, it was even an exaggeratedly acidic food since it was further acidified to account for the hypothetical lowest pH listed in food composition tables (but not seen in any of the brands investigated).

For experiments on crystal drinkware, the representative food was acidic white wine (pH 3.2), as explained previously. It should be noted that foods themselves contain a significant concentration of metals in their "natural" state, as shown in Table 5.

Table 5: background levels of metals in the reference foods a) in tomato sauce of pH 4.2 corrected to pH 3.5 and diluted 1:3 (µg/kg), b) in white wine, pH 3.2 (µg/kg)

food	Cd	Pb	Li	Al	Ti	V	Cr	Ni	Cu	Zn	Sn	Ba	Mn	Fe	Co
tomato	14	4	5	980	500	2.5	60	140	1300	1500	500	140	1250	4500	10
wine	0.1	9	6	1033	209	40	45	183	188	680	3	147	756	1037	35

3.1.1.3 Comparisons of testing methods for ceramics

For many items significant "article to article" variability was observed in the migration data. It was observed that it is necessary to use of at least four replicates for each migration experiment due to the heterogeneity of the samples that led to a large variability of data. thus the use of at least four items remains a must for testing compliance. The experimentation and full results are described in the individual specific report[16].

3.1.1.3.1 Testing modes (time/temperature/simulants)

A comparison between two simulants and the benchmark food (acetic acid 4 % for 24 h at 22 °C, citric acid 0.5 % for 2 h at 70 °C and hot tomato sauce) showed that migration of metals, in particular lead, was higher in either simulants than into tomato (Figure 5). The results also showed that the migration profile in acetic acid was more representative for the tomato sauce. This confirms that acetic acid is an adequate liquid to represent the worst foods and conduct compliance tests.

Practical considerations are important to identify an appropriate migration test that can be used routinely by both industry and control laboratories. In this context, the migration test at room temperature is easier to manage, it can allow the use a migration room as alternative to individual ovens thus a larger number of samples can be analysed in parallel. The test is less energy consuming, gives less risk of evaporation of the simulant (which influences results), and allows an easier control of temperature during tests

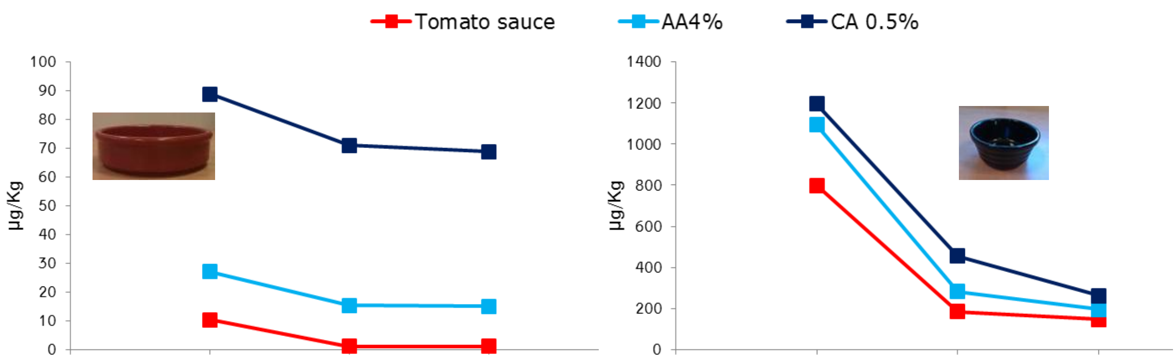
[16] Testing approaches for the release of metals from ceramic articles – In support of the revision of the Ceramic Directive 84/500/EEC, Beldi et al, EUR 28363 EN, doi:10.2788/402683

(including for the equilibration of the simulant), and less safety concerns than handling hot acidic simulants (especially for large volume articles).

3.1.1.3.2 Repeat testing

The results (Figure 5) showed that in general, the migration of lead decreased through the successive migrations. The relationship between the third and the first migration was however NOT always constant. The percentage of decrease in migration value from the first to the third migration was on average 75-80 % but it varied from 30 % to 94 % in 47 samples tested. This implies that prediction of values for the third migration based on the value of a first migration may NOT be derivable.

Figure 5: Typical types of migration profiles for migration of Pb from tableware into acetic acid 4 % (22 °C, 24 h), citric acid 0.5 % (70 °C, 2 h) and acidified tomato sauce. The successive three points on the graph represent migration I, II, III.



3.1.1.3.3 Effect of week-end lag phase in testing in repeat-use regime

The aim was to test whether the presence of a week-end between consecutive tests had an impact on the migration. This would imply that the tests would need to be started only on Mondays or Tuesdays to complete the third migration before a week-end. This is a relevant limitation in productivity for official controls and industrial laboratories.

A comparison was conducted on successive migrations where one of the migrations was separated by a week-end (between first and second, or second and third migration tests). The articles were left during the non-testing time with water or without water (empty) in order to assess which protocol would have the least effect compared to conducting 3 consecutive migrations of 3 successive days without gaps. The comparisons were conducted over a range of products to increase the confidence in drawing general conclusions (see individual report for full details).

The results with a 72h lag phase (representing a weekend) with the articles left empty, rather than filled with water, were more similar to 3 consecutive tests. No significant difference was observed between the two protocols.

This implies that testing is not subjected to start on certain days of the week, which means productivity can be maintained in repeat-use testing. For results found borderline of the limits, a confirmation test with true successive migrations would serve as validation.

3.1.1.4 Accelerated testing

The aim was to accelerate the migration process to minimise the length of successive tests without using a higher temperature. It consisted of increasing the acidity of the simulant, using a pre-treatment in acetic acid 10 % for 5 h at 22 ºC (aiming to represent migration I + II) followed by the standard test using acetic acid 4 % for 24 h at 22 ºC .

This accelerated test usually resulted in much higher levels than those obtained in the third migration with acetic acid 4 % (22 °C, 24 h) (current test 84/500/EEC). These results suggest that increasing the acidity in an attempt to substitute the first two migrations in repeat testing is not an adequate option

The development of accelerated test would require a more systematic underpinning research to generate clear relationships of the impact of acidity on the kinetics or mechanisms of migration for different metals.

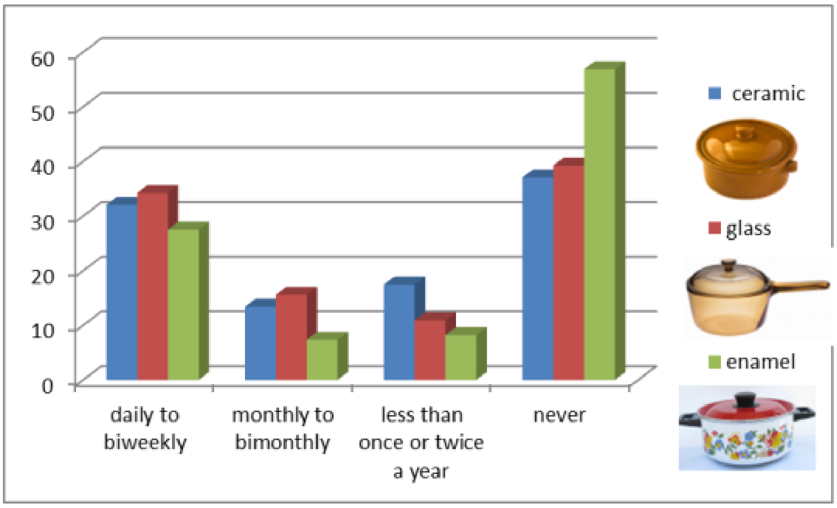
3.1.1.5 Survey on occasional use of tableware

The survey focused on what was perceived as occasional use for consumers for different types of tableware, crystalware and cookware.

For tableware, the results showed that for sets such as wedding or hand-decorated sets, close to 20 % of respondents considered them for daily to weekly use, compared to 80 % that considered them for monthly to yearly use. The handcrafted, artisanal and terracotta items were overwhelmingly considered as used once a year (or less or never, as decorative objects).

For cookware, the results indicated that consumers tend to have a predilection for one type (material) of cookware they will tend to use more. The individual replies leading to the distribution shown in Figure 6 suggested that people using ceramics will likely tend not to use glass or enamel This was not the case for bakeware where more types were reported to be used concurrently (ceramics, glass, metals). On average 30-40 % reported weekly use regardless of the material except for enamel used more rarely.

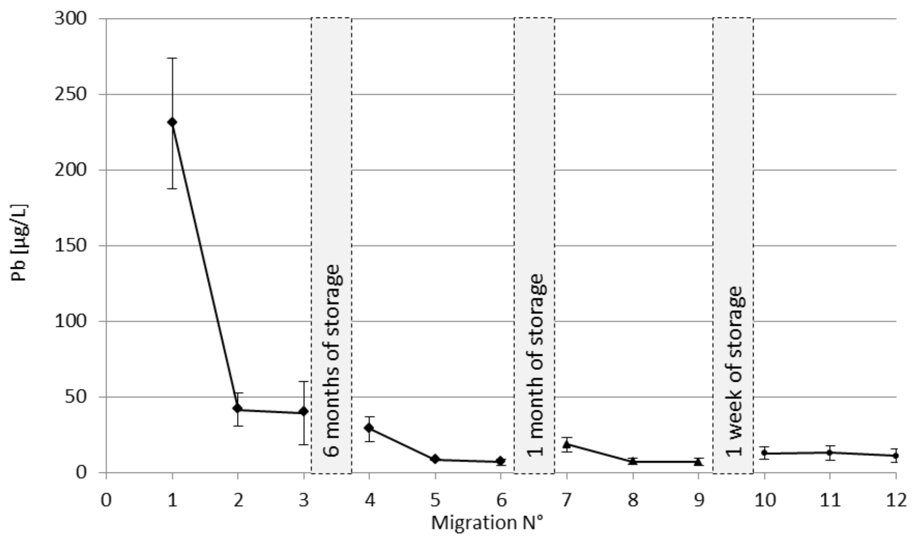
Figure 6: frequencies of use in cookware



3.1.1.6 Effect of storage (occasionally used articles)

The scope of this experiment was to evaluate and compare the effect of storage on migration of lead from ceramic articles. The results obtained showed that the majority of lead migrated in the first migration and its concentrations in the successive migration solutions even after 6 months of storage were always lower (Figure 7). Only in few samples the values in the first migration solution after 6 months of storage were slightly higher than those of the third migration of the previous test, but they were still far lower from those of the initial exposure to acetic acid 4 %. The nature and type of the sample had an important effect on the migration process. This indicated that the effect of storage between uses had relatively little effect on the migration values of repeated tests for ceramics, compared to the difference from the first migration vs. all successive ones.

Figure 7: Examples of profile for migration of lead after different storage times for samples with decorations



The results suggest that for articles used only a few times per year, if a repeated use regime would be implemented with three consecutive migrations, then this test regime could still be representative for occasional use in the case of ceramics.

3.1.1.7 Conclusions for ceramics

- In the context of lower limits, testing using repeat-use testing is indicated to mimic a long service life of multiple uses
- The test method using acetic acid (22 °C 24 h) is an adequate test condition
- Ideally successive migrations should be carried out with a lag phase between consecutive migrations of less than 1 h. The successive tests may have a longer gap between successive migration if a week-end is present between one migration and another. This does not have a major impact on the results and testing is thus not subjected to start on certain days of the weeks, which means productivity can be maintained in repeat-use testing. For results found borderline of the limits, a confirmation test with true successive migrations would serve as validation
- A longer storage (representing occasionally used articles) did not affect considerably the metals migration for ceramics tableware compared to the difference of using only one (first migration) as currently done under Directive 84/500/EEC. A repeat-use testing is adequate for a range of frequencies of use of tableware and remains an adequate convention even for seldom used articles for ceramics.

3.1.2 Migration testing from bakeware

Bakeware/cookware (category 3[a]) was also investigated under the scope of the project. For these articles, their normal conditions of use (heating acidic foods for prolonged periods) are conducive to higher migration of the metals into food.

Some standards[17] exist that imply the use of temperature with testing conditions such as hot (boiling) acetic acid solution of 4 % for 2 h. Due to the presence of acid fumes and boiling simulant, these types of tests pose serious safety concerns when applied routinely. Thus, testing at elevated temperature was discarded as an option and a conventional test using room temperature was chosen to perform studies.

[17] ISO 8391-1:1986, Ceramic cookware in contact with food -Release of lead and cadmium- (test method)

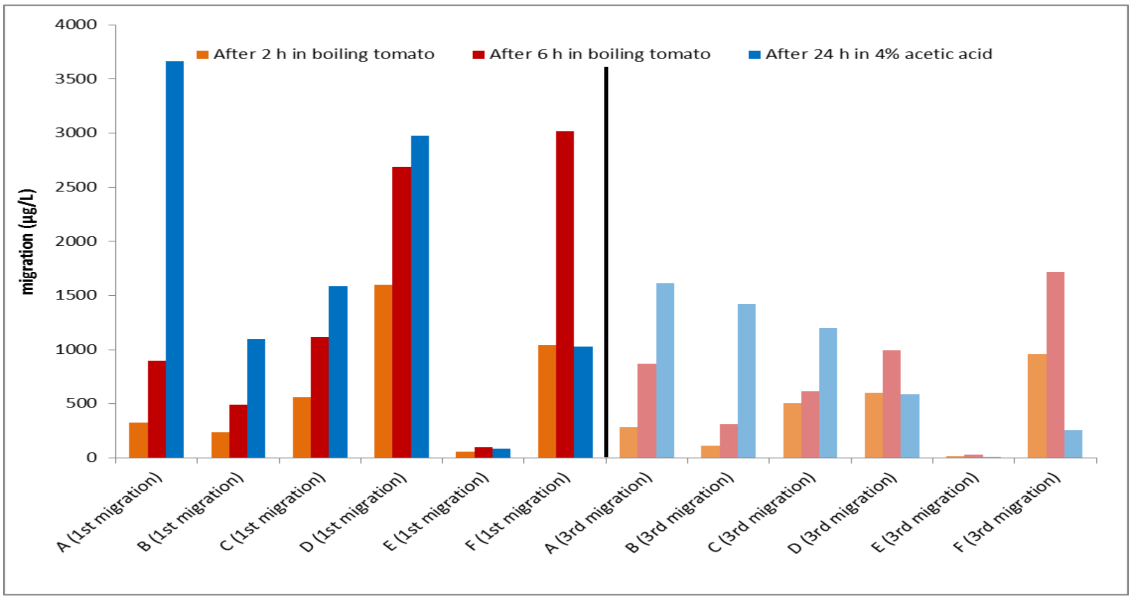
For bakeware, the study included both ceramic articles as well as a few (three) enamelled articles. They were all considered together since only a limited total sample set (n=20) was available (descriptions in annexes 1 and 2). The experiments included:

1) a comparison of using the conventional test for tableware (three consecutive migrations into acetic acid 4 % at 22 °C for 24 h)

2) a kinetic study of migration of metals (Pb, Cd, Co) into boiling tomato sauce (pH 3.5) over 6 h, at several time points. The kinetic study was conducted on six highly migrating samples. Three consecutive kinetics (of 6 h each) were performed over three days (repeat-use scenario).

Results revealed several profiles of migration into foods that pointed out to potentially complex migration according to different types of ceramics. As seen in Figure 8, the migration of lead in the first test in acetic acid after 24 h at 22 °C was always greater than after 2 h in boiling tomato sauce for all samples, and it was higher or than after 6 h in boiling tomato for more than half of the samples (left side of the bar graph for the six samples tested). The migration of lead in the third migration[18] in acetic acid after testing for 24 h at 22 °C was higher or comparable to the third kinetic in tomato sauce after 2 h of boiling in tomato sauce, for most samples but not all, and it was not always higher than after 6 h of boiling in tomato sauce (as shown by the bar graphs of the six highly migrating samples on the right hand side illustrating the third migration).

Figure 8: comparison of values between kinetics in boiling tomato and after conventional test in acetic acid



This means that for bakeware/cookware, the first migration gives a good assurance of being worst case. In some cases it can be much worse than the food would ever be. The third migration for the samples tested showed values more proportional to those in tomato but could also be lower than a 6 h simmering in tomato sauce.

As the set of samples received was quite limited, further work could be carried out on a larger set of samples to evaluate the adequateness of the release test in acetic acid 4 % without use of temperature under repeated use regime. It would require the collection of appropriate ceramic articles containing other metals beyond lead.

[18] The second migration is not shown in this synthetic report for clarity and simplification purposes.

3.1.3 Method for testing migration of rim

Currently there is no specific provision stipulated in the EU legislation for testing the migration from the rim of hollowware articles. An internationally agreed test is therefore of relevance for the potential development of limits also for the rim. Test methods were compared on series of different articles of varied nature.

3.1.3.1 General comparison of test approaches

Different test methods were first compared similarly to the approach taken for ceramics. This meant comparing migration from the rim into acetic acid 4 % for 24 h 22 °C, into white wine (pH 3.2), and into citric acid 2 h 70 °C (considering a hot fill of some drinks). The results indicated that the citric acid in hot testing conditions led to similar results compared to the simulant acetic acid at room temperature. The experimentation and results are described in details in the corresponding individual report[19]. The test using acetic acid 4 % remained adequate and was more severe than an acidic white wine, especially in the first migration, or slightly worse / comparable to wine, especially for the third migration.

3.1.3.2 Comparison of the existing specific standards

The planned focus was on lead and cadmium, but also included other metals where applicable to increase the breadth of the investigations. Two official protocols were compared on all samples for which the test of the rim could be applicable.

The rim area was tested using two different approaches with and without the use of paraffin wax in the conventional 4 % acetic acid simulant (22 °C, 24 h). The norms ISO 6486-1 and EN 1388-2 use wax on the non-tested portion of article, whereas the ASTM C927-80 standard does not. In the ISO and EN standards, melted wax is used to cover the non-tested portion of the article, whereas in the ASTM Standard, the samples are immersed in the simulant upside-down into a beaker without the use of melted paraffin wax (Table 6). Limits are present in the ISO 4531-1/2:1998 standard as 2.0 mg/article for lead and 0.2 mg/article for cadmium.

Table 6: existing norms for the rim test

Standard name and principle	Illustration
ISO 4531-1/2:1998 and EN 1388-2:1995 (surface not tested is covered with paraffin wax for testing)	
ASTM C927-80 (surface not tested is left uncovered during testing)	

The migration of metals from nine samples (both industrial and ad-hoc manufactured samples) was investigated. The test with wax was carried out only on samples (ceramic and glass) which presented a greater migration of metals better suited for comparison.

The results of this comparison are illustrated in Figure 9. It shows for a typical sample the results for lead (bar graph on the left) and for cadmium (bar graph on the right). On average, another three or four metals were found in detectable amounts beyond lead and cadmium, and included for example most commonly iron, aluminium, barium, nickel,

[19] Peltzer et al., Scoping investigations on the release of metals from the rim area of decorated articles (in support of the revision of Ceramic Directive 84/500/EEC), 2015, EUR 27178 EN, doi: 10.2788/484454

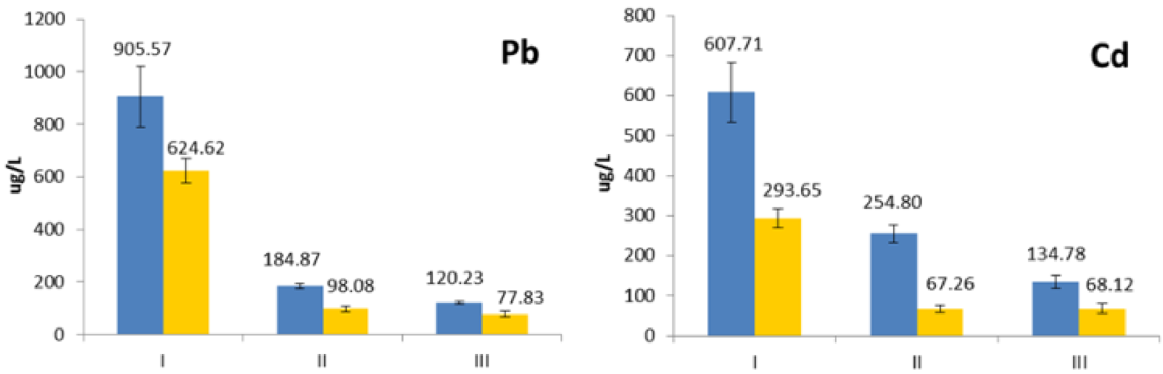
more rarely titanium, lithium, cobalt, manganese. In the graphs shown, for each sample, each bar represents the average of values of four independent test specimens, and shows the deviations of the results. The blue bar represents results for a rim test using a protocol ASTM (without wax), and the yellow bar represents results of a rim test using the ISO/EN protocol (with wax). The graphs also show the results of the first (I), second (II) and third (III) successive migrations.

The results indicated a slight difference between the ISO and ASTM standards. The method with paraffin wax was generally slightly less severe than the method without, likely due to the fact that the area not in contact with the simulant was protected from the acidic vapour that could condense on the surface of the sample to extract more metals. The difference was most relevant for the first migration, but much less for third migration. In some samples it seemed that the presence of wax allowed to reduce a little the standard deviation between test specimens, but it was not statistically relevant.

From the standpoint of the samples used in the study, migration of lead occurred from all the samples tested. It was also possible to detect limited migration of cadmium and other metals from the rim area of decorated articles.

It was observed that the migration of lead, cadmium and other metals generally decreased in successive migrations. Highly decorated articles with very bright colours led to a greater migration of metals. The migration of elements from test articles into white wine was always lower than that into acidic simulants.

Figure 9: Effect of the type of rim test on 3 successive migrations (example of lead and cadmium shown on one typical sample as illustration)



A point for deriving consensus was also to obtain feedback of users. A questionnaire was sent to the NRLs and to the stakeholder group on the use of the rim test in routine analysis. The responses indicated that about 64 % (24/37) of respondents were already performing lip/rim tests, of which 79 % (19/24) indicated to use the paraffin wax (i.e. EN1388-2:1995 and ISO 6486-1 standards). Consequently articles that are decorated undergo two tests: the normal migration testing, and since these articles have a decorated rim, they are also subjected to the rim test that specifically tests a portion of both inner and outer surface.

3.1.3.3 Conclusions for the rim test

— The test that used melted wax on the non-tested area generally gave lower migration of metals into food simulants and could be more realistic, but the standard deviations of the results do not indicate a very significant statistical difference.

— Both tests are adequate and both present the ability to be implemented /adopted for testing. From a usage standpoint, the ISO/EN standard using melted wax (ISO 6486-1/EN1388-2:1995) is already in use by a significant majority of tests and controls laboratories in routine tests.

3.1.4 Method for testing migration from crystal

In the European Union, labelling of "crystal glass" products is regulated by Council Directive 69/493/EEC[20]. This directive defines four categories of crystal depending on the chemical composition and properties of the material: 1) Superior crystal PbO ≥ 30 %; 2) Lead crystal PbO ≥ 24 %; 3) Crystal glass superior or crystallin ZnO, BaO, PbO, K_2O singly or together ≥ 10 %; 4) Crystal glass BaO, PbO, K_2O singly or together ≥ 10 %.

While many studies have been conducted on the migration of metals from ceramics, much fewer have investigated the migration of heavy metals from crystal glass in contact with foodstuffs or food simulants. The migration of metals from crystalware depends on factors such as composition, pH, temperature, physical properties of the food and time of contact. Currently there is no specific provision stipulated in the EU legislation for crystal.

The planned focus was lead considering the nature of the products. Testing methods were developed for crystal ware, which were compared to testing on food itself. In this case white wine as used for drinks. The aim was to develop conventional tests that can be worst case scenario, but remain in line with exposure and with pragmatic protocols from a laboratory standpoint.

The experimental scheme developed included multiple-use tests on wine and on simulants. It also included a study of longer term storage on lower frequency of use. The migration from 15 samples of crystalware was investigated with respect to migration of metals in different conditions from different samples. The experimentation and full results are described in details in the corresponding individual report[21].

3.1.4.1 Comparison of test migration regimes

For all samples included in the study a relevant migration of lead was observed. Few other metals were found in migration solutions which included zinc, antimony, barium and silver.

The migration of lead, cadmium and other metals decreased in successive migrations. The extent of the third migration depended on the metals considered and potential damage of the heterogeneous decoration of the articles during the exposure. Overglaze and highly decorated samples were understandably more sensitive to exposure to acidic food simulants and migration of metals occurred to a greater extent than in the case of test articles with underglaze decorations.

3.1.4.1.1 Comparison of different testing modes

Two test regimes were compared. The first one, currently in use for ceramic, uses acetic acid 4 % for 24 h at 22 °C. It was repeated three times to represent repeated use. An alternative approach with citric acid 0.5 % for 2 h at 70ºC, also for three consecutive migrations, was also used (to keep a comparison with tests done on ceramics).

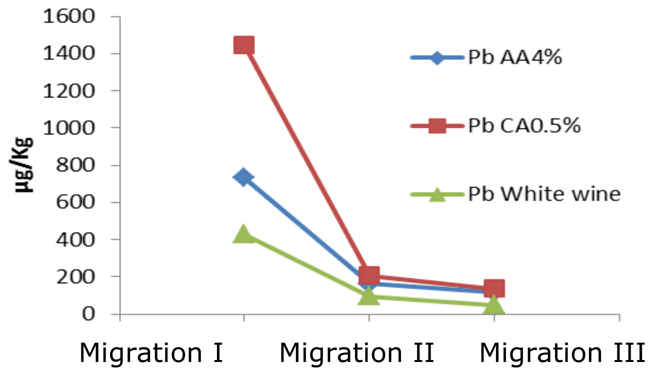
The results showed that the migration of lead was higher in the two simulants compared to the white wine (Figure 10), most notably in the first two migrations. The test using citric acid (at higher temperature and shorter time) led to more extreme results and was considered disproportionate especially in the first two migrations.

The results in standards conditions 24 h at 22 °C were all above the DSVs of lead (10 µg/L) and will pose trade issues for crystal articles producers. The migration of elements from these conditions were found to be exaggerated compared to normal conditions of use and led to further studies to find a more adequate time temperature exposure.

[20] 69/493/EEC, Council Directive of 15 December 1969 on the approximation of the laws of the Member States relating to the crystal glass. OJ, L326:p. 599-602 (1969)

[21] Peltzer et al, Scoping study on the release of metals from crystalware (in support of the revision of Ceramic Directive 84/500/EEC), 2015, EUR 27180 EN, doi:10.2788/885263

Figure 10: Lead Crystal– Typical migration profile of Pb in acetic acid (AA) 4 % 24 h at 22 °C, hot citric acid (CA) 0.5 % 2 h and white wine (WW) 24 h at 22 °C.

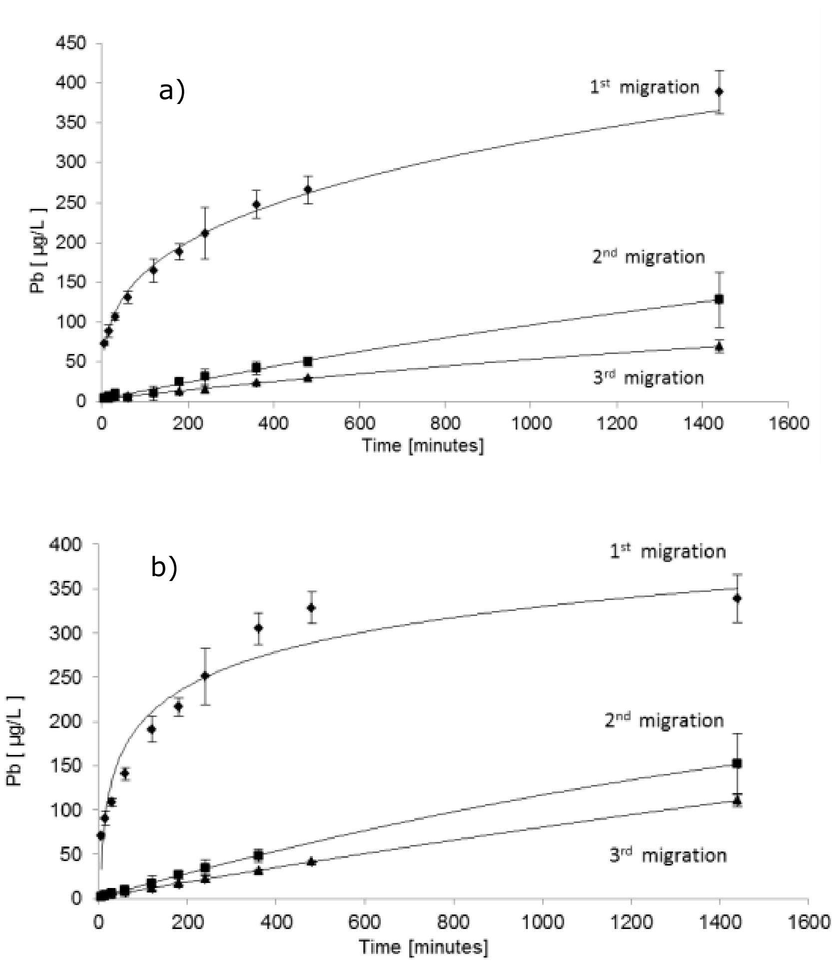


3.1.4.1.2 Kinetics experiments

Further investigations compared kinetics on both food (wine) and simulants to derive more appropriate testing approaches. Kinetics of migration were generated in 4 % acetic acid and in white wine for different periods of time from 5 min to 24 h, and repeat testing (3 consecutive migrations). These were done on 4 different types of crystal articles.

The results showed that the kinetics of migration of lead from crystal exposed to acidic liquids especially for the first migration is quite rapid and steady over time (Figure 11). The second and third migrations were much lower than the first one (therefore likely to be more representative of the article as a whole).

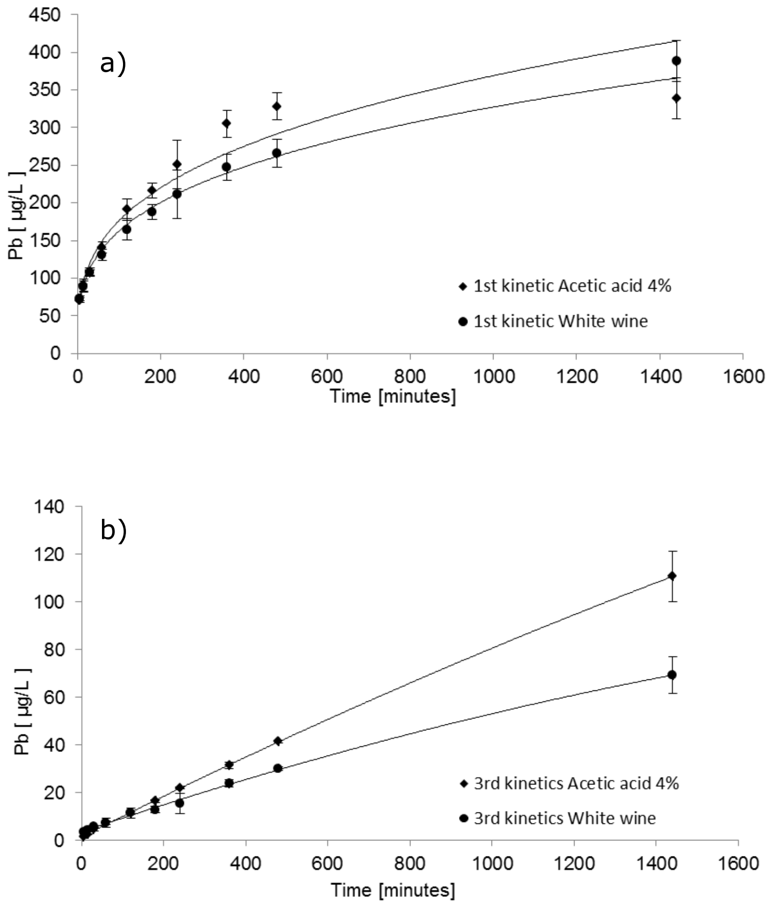
Figure 11: Consecutive kinetics in a) white wine and b) acetic acid 4 %



The results were comparable in acetic acid and white wine: in the first migration (first kinetic), the migration of lead after 2 h was ca. 60 % of the total migration after 24 h for acetic acid and ca. 50 % for wine. In the third migration (third kinetic) the migration of lead after 2 h was around 10-11 % of the total lead migration after 24 h for both. Overall, for the course of the entire 24 h at 22 °C, the results obtained for acetic acid 4 % were generally higher than those in white wine. In the first migration, the migration in acetic acid 4 % was already slightly higher than in white wine (Figure 12a). In the second and third kinetics (Figure 12b), the higher migration in acetic acid vs. wine became more notable. This confirmed previous studies noting that lead migration decreases with increasing pH and ethanol content[22]. The pH of acetic acid 4 % being 2.3 vs. 3.2 in wine, its lower pH makes it an adequate simulant worst than the wine matrix.

Acetic acid 4 % is an adequate simulant remaining worst case than the wine matrix, and more generally speaking also than alcoholic beverages.

Figure 12: Migration of lead in white wine and acetic acid in a) first and b) third kinetic



3.1.4.2 Attempt to adjust testing mode to a more representative exposure

One issue of the test using the same conventional conditions as for ceramics is that the conditions of 24h at 22 C are not representative of the actual use of the articles. Indeed, it is most unlikely that the type of beverage drunk from crystal glasses such as a (wine, champagne etc.) would remain in its glass for 24 h. This led to the conclusion a specific test was needed to mimic the worst case of actual exposure.

[22] ILMC ceramic Handbook, Lead Glazes for Ceramic Foodware , Research Triangle Park, North Carolina, International Lead Management, Inc., (2002)

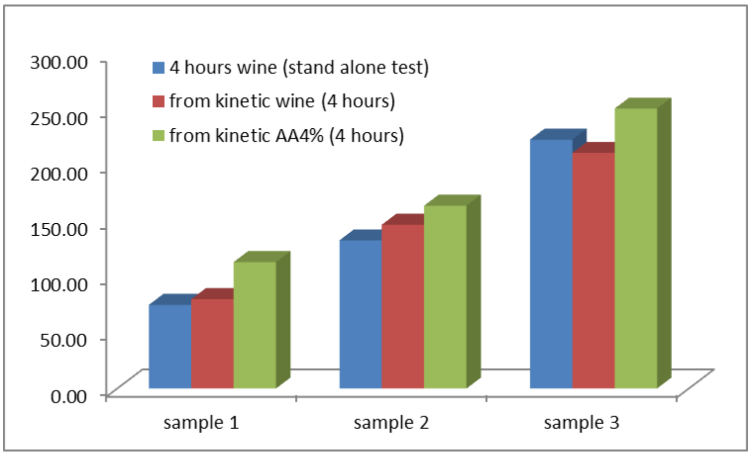
On four samples, a kinetic was done to mimic daily use of exposure to wine. The glasses were filled with wine, exposed 1 h and the liquid analysed. They were washed, rinsed and left to dry. The next day the same 1 h exposure to wine was repeated and analysed. This was done seven days in a row. Figure 13 illustrates the results.

Figure 13: migration 1 h in wine, daily for seven days (four samples shown).

The figure clearly showed the similar drop in value between the first migration (exposure) and the following ones. It also showed that the values from the third migration on to the seventh –eighth time remained almost constant. This indicates that for testing articles that have a service life of multiple uses, repeat testing is the most indicated and three successive migrations are appropriate.

A comparison was done between a 4hr test in wine (part of a kinetic experiment or single test), and in acetic acid. This is shown in the first migration (Figure 14).

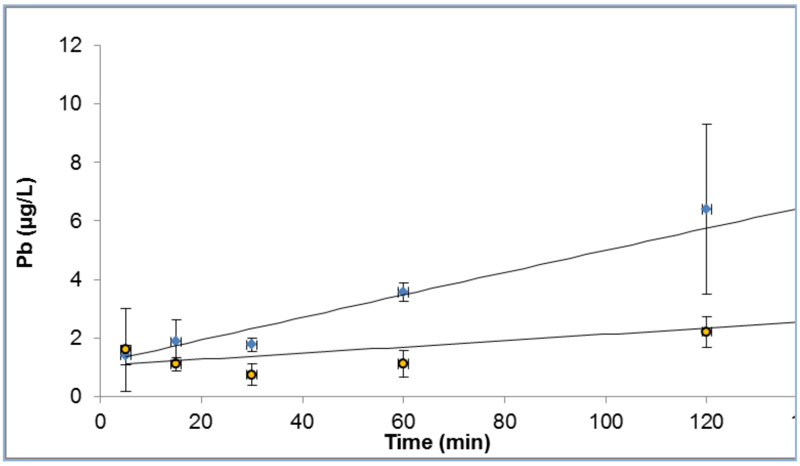
Figure 14: comparison of the standalone 4 h test in wine, vs. the kinetics in wine and the kinetic in acetic acid (at 4hr), for the first migration.



The results indicated again that the acetic acid is more stringent than the wine, and that the two experiments on 4 h migration in wine are quite consistent. It can thus be assumed confidently that acetic acid can represent a worst case wine and the time of exposure can be chosen as relative value. The time of 4 h was subsequently found by the stakeholder group too excessive as representation of worst case exposure, since it is quite unlikely that people would consume wine poured in a crystal glass which would be left untouched for 4 h and then ingested. It was concluded that a 2h test would be more appropriate. The kinetics of successive migrations in wine were examined as a more systematic comparison and model. The focus was on the 2 h time point. The yellow dots are for the wine and the blue for the acid simulant. The graph is shown for the third migration (Figure 15).

The results indicated that the values in acetic acid were similar yet above the migration in wine.

Figure 15: kinetics of the third migration in wine vs. acetic acid (focusing on 2 h)



This means that a 2 h test using 4% acetic acid in repeat-use has the potential to be an adequate migration test for crystalware

3.1.4.3 The case of occasional use of crystalware

The aim was to answer the question of what is the impact of storage or occasional use of certain articles on the migration of metal in conventional testing for occasional use.

3.1.4.3.1 Survey of use

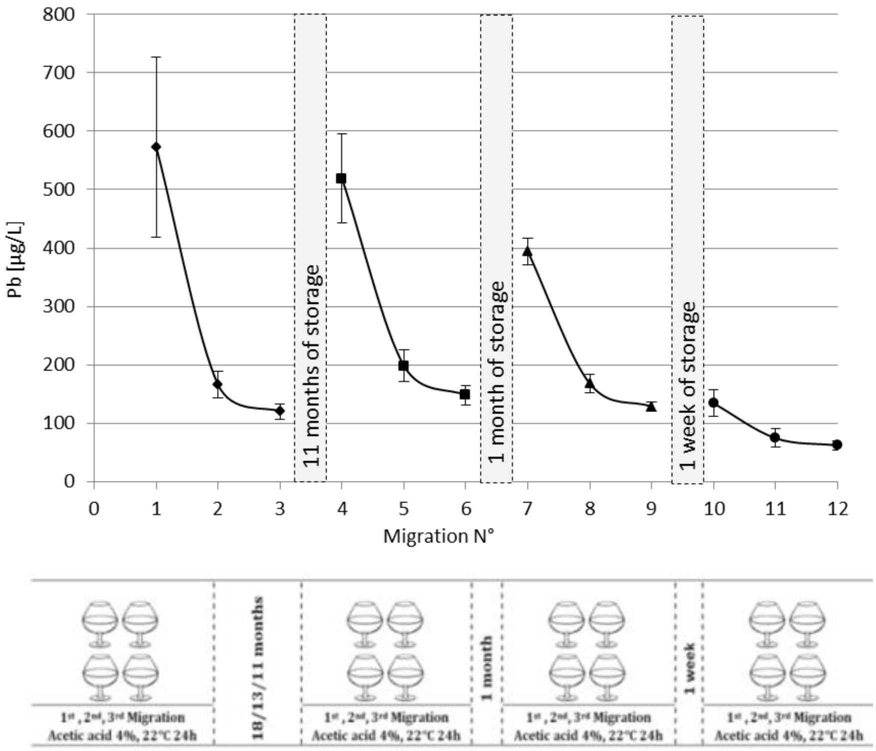
A survey was conducted on perception of frequency of use. For 29 % of respondent, the frequency of use of crystalware stemware was never, while for 31 % once a year, for 10 % every six months, for 8 % every three month, for 8 % once a month, for 10 % weekly or biweekly and for 4 % daily. For whisky glasses the survey indicated that 51 % of respondents never used crystal, and 16 % once a year. The rest of frequencies were each around 5 %. Decanters were never used (i.e. used only as decorative objects) by 31 % of respondent, and used to store liquids up to a year by 8 % of respondent and up to 6 months by 5 %. The remaining categories of storage time were less than 1 % each. Considering the high percentages of lower frequency of use, it was of interest to investigate the effect of long storage on the migration of lead.

3.1.4.3.2 Effect of storage on migration of elements for crystal

Different types of crystal articles were used. The conventional migration test of 24 h at 22 °C with acetic acid 4 % was applied but under repeated use regime, i.e. 3 consecutive migrations. After various storage times (no contact with food simulant) ranging from one day to 18 months, the migration tests were repeated. Lead was quantified.

The effect of storage between uses has a marked impact on crystalware. The results showed trends for crystal different from ceramics, indicative of a different migration mechanism (Figure 16). There was an increase of lead migrated if storage was present in between tests. The migration of lead upon successive testing/migrations becomes hindered by the formation a silica enriched layer that reduces the diffusivity of lead ions. Upon storage this layer tends to deteriorate and disappear. Consequently the lead values of the first migration after a storage period are much higher. This is most notable after a one year storage but is already visible after one month.

Figure 16: Pb migration after different storage time representative for crystal glasses



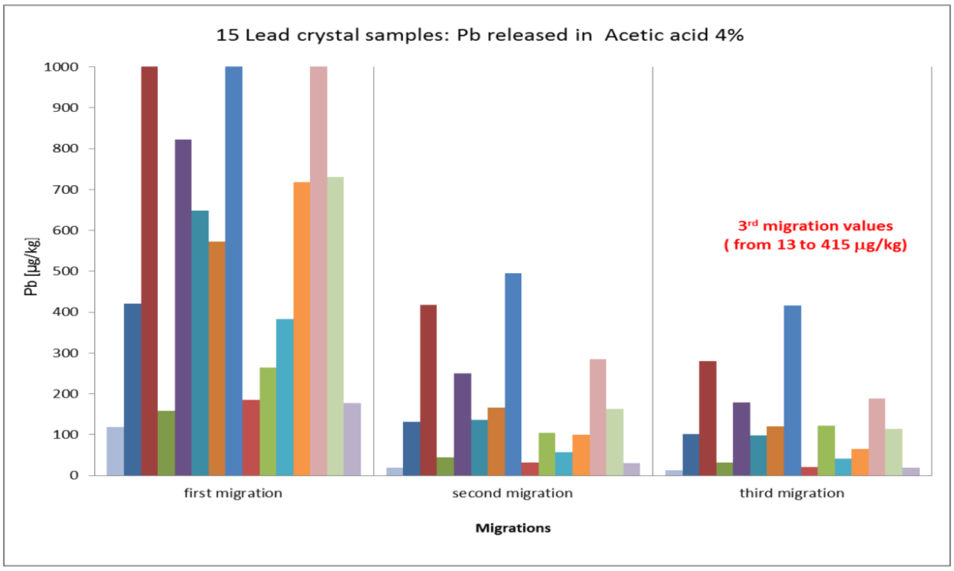
For articles used only a few times per year, the repeated use regime with three consecutive migrations is less representative depending on the frequency of usage.

The effect is most notable for yearly use and starts appearing for less than monthly. The effect is mostly on the first migration (the third migration much less sensitive). The test 2 h 22 °C could be applied with a value on the first migration for occasional use

3.1.4.4 Relation of migration from the type of products versus potential DSVs

The results for all samples were plotted to summarise the migration of specialty glassware such as crystal. This was based on the original study using 24 h at 22 °C (Figure 17).

Figure 17: Results of the first (I), second (II) and third (III) for the crystal samples.



The results indicate that the DSV would be exceeded greatly in a test using 24 h at 22 °C. However, since the exposure was found unrealistic and adjusted to 2 h, the previous section would roughly indicate that for a 2h test, the results of the first migration would be approximately 50 % of the values shown on the graphs.

This would still place this niche market at a major risk from a trade standpoint.

The third migration cannot really be directly compared as the second/third migration in Figure 17 come after a full 24 h first migration, which would not be the case for a 2 h repeat test. From the graph and on the 15 samples tested, values in the third migration ranged from 13 to 415 µg/kg and averaged at 120 µg/kg. Results of a 2h repeat tests done on a very limited number of samples still available (n=4, data not shown), place the third migration at values of 15-43 µg/kg with an average of ca. 30 µg/kg.

Consequently, from a migration standpoint and from a testing perspective, the repeat testing is indicated with lower limits for daily use, whereas for articles stored longer than a month, the crystal tend to "replenish" itself to a higher migration. In this case an attention to the value of the first migration would also be appropriate to consider.

3.1.4.5 Conclusions for crystal

— Acetic acid 4 % is an adequate simulant for testing articles both for single use or worst first migration, or for a service life of multiple uses in third migration.

— The exposure time of the simulant can be chosen as the exposure time of the wine as they have a comparable mechanistic effect on the migration of lead from crystal. A test of 2 h in acetic acid is adequate in severity

  - To represent the 2h exposure in wine, which the expert workshop considered as a fairly worst case.
  - To account for slightly longer exposure, since the kinetics of migration are quite fast in the first migration.
  - To perform in repeat-use (third migration) to account for daily use
  - To be completed in one day, thus maintaining productivity.

— The effect of storage between uses has a marked impact on crystalware. For articles used only a few times per year, the repeated use regime with three consecutive migrations is less representative depending on the frequency of usage.

— For articles that tend to be stored, the value of the first migration (to a higher level considering the lower exposure) could be considered.

3.2 Analytical method for the quantification of metals

Method detection limits (LOD) were calculated from the standard deviation of the blank from 10 determinations. The LODs are reported in Table 7. It shows that the state of the art techniques are well capable to quantity low levels.

Table 7: LOD values in µg/kg for different simulants

Conc. [µg/kg]	Li	Al	Mn	Cu	Ti	Co	Zn	Cd	Ba	Pb	Zr	Fe	V	Ni	Cr	Ag	Sn	Sb	As
Acetic Acid 4 %	0.05	0.55	0.15	0.10	0.10	0.11	8.21	0.01	0.04	0.26	1.87	2.92	0.11	0.19	0.06	0.04	0.54	0.01	0.09
Tomato sauce	0.42	65.6	11.8	11.8	32.3	0.04	16.9	1.85	10.9	3.01	0.05	9.19	1.49	5.38	1.78			0.09	0.04
White wine		15.83	15.90	2.28	65.03	0.11	15.34	0.07	7.13	0.31		41.65	1.75	0.53	1.38			0.05	0.03

Two ILCs were conducted according to international standards and robust statistics. They included more than 50 laboratories from 27 countries for each exercise. They included national reference laboratories, official control laboratories, and invited expert laboratories. A first interlaboratory comparison in 2014[23],[24] was used to generate a full method protocol, which was also given to the standardisation group ISO TC166 WG3 on ceramics. Precision criteria were also derived for each method. It was found that the relative repeatability standard deviations were very low generally less than 2 %. Relative reproducibility standard deviations for lead were around 10 % for ICP-MS and ICP-OES techniques rose to 16 % when graphite AAS technique was used. Relative reproducibility standard deviations for cadmium were around 5 %, 10 % and 20 % using respectively ICP-MS, graphite AAS or ICP-OES techniques. For other elements the relative reproducibility standard deviations were for most of the cases less than 10 %.

The data was then clustered to evaluate whether different instrumentations lead to different results (Table 8). It was found that the analytical techniques (ICP-MS, ICP-OES, graphite AAS) were generally equivalent and not significantly different for almost all elements and samples investigated[25].

Table 8: Statistical evaluation of performance of instrumental techniques for the different elements quantified

DIN 38402 A45/ISO 5725-5							
Sample	C2						
Element	Ba	Co	Mn	Pb	Cd	Ni	Al
ICP-MS/ICP-OES Test decision	equivalent and no significant differences	equivalent and no significant differences	equivalent and no significant differences	equivalent and no significant differences	equivalent and no significant differences	equivalent and no significant differences	equivalent and no significant differences
ICP-MS/AAS Test decision	-	equivalent and no significant differences	equivalent and no significant differences	equivalent and no significant differences	equivalent and no significant differences	equivalent and no significant differences	-
ICP-OES/AAS Test decision	-	equivalent and no significant differences	equivalent and no significant differences	equivalent and no significant differences	equivalent and no significant differences	equivalent and no significant differences	-

A further ILC was organised in 2016[26] at EU level to assess (i) the analytical abilities of participating laboratories to quantify metals (Ba, Co, Mn, Pb, Cd and Al) in a solution of acetic acid 4 %; (ii) the performance of laboratories to carry out the migration test on ceramic and glass articles and (iii) to derive precision criteria, including repeatability and reproducibility for the overall migration test of elements from tableware.

The rate of success was almost always higher than 80 % for all elements in all samples. The final exercise evaluated how well laboratories could estimate the uncertainty of their measurement. This assessment indicated a need of an improvement in this regard.

Conclusions on the analytical determination:

— The ILCS allowed to assess:

— The satisfactory competence to determine Pb and Cd at low concentration levels (10 and 5 µg/kg) in migration solutions in two separate ILCs of increasing severe target for repeatability and reproducibility

— The satisfactory competence to determine Ba, Co, Mn, Ni, As and Al potentially migrated from ceramic articles in migration solutions

— The establishment of precision criteria including reproducibility and repeatability standard deviations for the quantification of metals in acidic migration solutions using different analytical techniques: ICP-MS, ICP-OES, graphite-AAS

[23] Report of Inter-laboratory comparisons - ILC 04 2014 – Ceramics, 2016, Beldi et al, doi: 10.2788/1849
[24] Precision criteria of methods for the quantification of metals, 2016, Beldi et al, doi:10.2788/592775
[25] No data reported for Ba and Al for AAS because only one laboratory used AAS thus it is not possible to compare statistically
[26] Report on the inter-laboratory comparison exercise -Determination of elements in acetic acid solutions and in migration from ceramic and glass tableware, 2017, Jakubowska et al, EUR 28690 EN, doi:10.2760/573036

— The equivalent performance of several instrumental techniques for the elements and samples included in the exercises.
— The satisfactory performance (precision criteria) of the test of migration of elements under repeated use regime from tableware including decorated glass and ceramic.

Therefore, overall, ICP-MS is a suitable technique and allows to reach limits of detection and quantification adequate for compliance and enforcement for lead, cadmium and other metals potentially migrated from ceramic and glassware. Other techniques such as ICP-OES and graphite-AAS are also adequate. The performance of enforcement laboratories is satisfactory for the quantification of metals toward lower levels for lead, cadmium and for other metals.

4 Conclusions

The JRC research evolved to a much larger and complex project than initially foreseen, but was rich in data that can be used not only as indicators of the technical feasibly to lower limits, but also to broaden the level of harmonisation possible for the ceramics and glass sectors. The full overview is presented in Annex 1.

For ceramics tableware

Overall, the results show that a migration test following the protocol set out by Directive 84/500/EEC is realistic when this protocol is modified to use the results of the third migration rather than the first migration. The approach is still conservative but close to the migration that can be expected into foods. This modified protocol is technically straightforward while the testing cost would remain in the same order of magnitude. Therefore, there are now no further scientific or technical hurdles to lower the limits.

The study posed a number of questions which could be answered.

On repeat-use testing to simulate the multiple use of tableware:

- When the limits are based directly on health considerations, they should more adequately reflect the migration that can occur in repeat-use scenarios.This can be simulated adequately by three successive tests.
- The repeat testing presents an advantage of less variability of results between replicate samples at second and third migration.
- The performance of migration tests (migration + quantitation) at lower levels for different metals is adequate as shown by two interlaboratory comparisons of increasing complexity (quantification and migration + quantification)

On the type of simulant and testing protocol to simulate the what happens with the worst foods:

- The conventional test regime using acetic acid at 22 °C for 24 h remains adequate
  - The test compares well to conditions of use to a worst case (acidic) food
  - The test works and compares well in severity both for a single migration test or in multiple successive migration tests
  - The migration in successive tests (e.g. 1,2,3 migrations) mimics well repeat-use for ceramics
  - The test is more adequate and more practical than alternative tests such as those proposed for coated metals using citric acid under hot conditions.
- The impact of an interruption of testing between migration when a week-end interrupts the repeated use testing protocol can be considered negligible
- Accelerated tests cannot be used at this stage by using stronger acids for shorter time to make a repeat-use testing more rapid. This option requires a much greater mechanistic understanding of migration.

On methods for testing of the rim of decorated articles

- The methods for testing the rim are both adequate and compare well in severity.

For bakeware

- The migration of metals from bakeware
  - Appears complex under exposure conditions of use (e.g. boiling tomato)
  - The present data does not clearly support any testing protocol to mimic migration at low temperatures.

— It is preferable to use test using room temperature for safety and energy reasons.
— The test on bakeware is already performed in a significant number of laboratories doing controls (24/37), for which an overwhelming majority (22/24) uses a test using acetic acid at 22 °C for 24 h.
— The data indicates that using acetic acid at 22 °C for 24 h remains adequate in the first migration and also in the third migration for the majority of samples tested
— It should be noted that data set was limited (limited number of samples) and exhibited a large diversity of behaviours, making conclusions quite difficult.

For crystal

— With respect to occasional use scenarios, the impact of storage on the migration of metal in conventional testing is barely observable for ceramics, but clearly observed in crystal.
— The test protocol used for crystalware was developed to respond to its specificity of use. The same simulant as that used for ceramics is adequate. A shorter time and a consideration of both the first and the third migration each with their own limits is a valid option.

On quantification and analytical methods

— The current analytical methods can quantify lower levels for lead and cadmium in simulant solutions and of a variety of other metals
— Several instrumental methods present a satisfactory performance at lower limits for different metals. The state of the art recommended in terms of performance and breadth of metals analysed in one rune is the technique of inductively coupled plasma mass spectrometry (ICP MS).

On this basis, the Commission may be reflecting on appropriate next steps to reduce the migration/migration levels for heavy metals from ceramic food contact materials in order to ensure a high level of consumer health.

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List of abbreviations and definitions

AA	Acetic Acid
ASTM	American Society for Testing and Materials
CA	Citric Acid
CEN	European Committee for Standardization
DG SANTE	Directorate-General Health and Food Safety
DSV	Discussion Starting Value
EC	European Commission
EFSA	European Food Safety Authority
EU	European Union
EURL	European Union Reference Laboratory
FCM	Food Contact Materials
GF-AAS	Graphite furnace atomic absorption spectrometry
ICP-MS	Inductively coupled plasma – mass spectrometry
ICP-OES	Optical emission spectrometry
ILCs	Interlaboratory comparisons
ISO	International Organization for Standardization
JRC	Joint Research Centre
NRLs	National Reference Laboratories
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
SRL	Specific Release Limit
TS	Tomato sauce
WW	White wine

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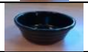
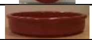
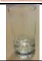
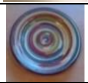
Annexes

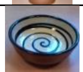
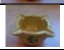
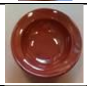
Annex 1. Samples and tests performed

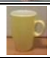
Type	Anon. code	SAMPLE	Description	N° of items	Diameter [cm]	Simulant vol.[mL] (internal vol.)	tests done by: NRLUK	NRL DE	NRL BE	JRC	type of test comparisons performed: acetic acid 4%	citric acid 0.5%	Tomato puree pH3.5	White wine	Rim (AA 4%; CA 0.5%)	Rim AA 4% Wax-no wax	Accel. test
Ad hoc	315G09		Glass decorated bowl: test for ILC 2016: not enough Pb and Cd for ILC exercise	4	16.5	280				X	X						
Ad hoc	315G09		Glass decorated bowl : Official Samples for ILC2016	300	14.5	350				X	X						
Ad hoc	315G10		Glass decorated bowl test for ILC 2016 : not enough Pb and Cd for ILC exercise	4	11.5	350				X	X						
Ad hoc	613C03		Porcelain coffee cup overglaze decorated (inside and outside)	92	6	110 rim test (50)		X		X					X	X	
Ad hoc	613C04		Porcelain coffee plate overglaze decorated	92	10	20	X	X	X	X	X	X	X				
Ad hoc	613C05		Porcelain coffee plate underglaze decorated	92	10	20	X	X	X	X	X	X	X				
Ad hoc	613C06		Porcelain coffee cup underglaze decorated (inside and outside)	92	6	110 rim test (50)		X		X					X	X	
Ad hoc	613G03		Glass soup plate decorated; High release sample made especially for the project.	50	21	250				X	X	X	X				
Ad hoc	613G04		Tumbler decorated outside with ceramic glass enamel; high release sample made especially for the project.	50	8	80 rim test (320)				X				X	X	X	
Ad hoc	613G05		Tumbler decorated outside with ceramic glass enamel; high release sample made especially for the project.	50	7	100 rim test (320)		X		X				X	X	X	
Ad hoc	613G06		Tumbler decorated outside with ceramic glass enamel; high release sample made especially for the project.	50	6.5	120 rim test (400)				X				X	X	X	
Ad hoc	616C21		Porcelain coffee cup on-glaze decorated; produced for ILC01 2016	300	6	55				X	X						
Bakeware	1015C01		Brown terracotta dish (cassolette)	34	13.5	250				X	X						
Bakeware	1016C02		Cast iron cookware	9	20	2250				X	X						
Bakeware	1016C03		Steel sheet (enamel) cookware dish	12	17.5	1350				X	X						
Bakeware	1016C04		Steel sheet (enamel) oventray	12	41*32	4000				X	X						
Bakeware	416C28		Porcelain red oven bowl	12	13	400				X	X		X				
Bakeware	416C29		Porcelain blue oven dish decorated inside (grey)	12	31*20	2000				X	X						
Bakeware	416C30		Porcelain blue oven dish	12	21.5*12.5	350				X	X		X				

							tests done by				type of test comparisons performed						
Type	Anon. code	SAMPLE	Description	N° of items	Diameter [cm]	Simulant vol.[mL] (internal vol.)	NRLUK	NRL DE	NRL BE	JRC	acetic acid 4%	citric acid 0.5%	Tomato puree pH3.5	White wine	Rim (AA 4%; CA 0.5%)	Rim AA 4% Wax-no wax	Accel. test
Bakeware	416C31		Porcelain blue/white oven dish	12	21.5*12.5	350				X	X						
Bakeware	713C015		Terracotta brown small bowl	20	8	not specified			X		X	X					
Bakeware	713C016		Erthenware black bowl	22	12	200				X	X	X	X				X
Bakeware	713C02		Terracotta brown small bowl	20	9	100				X	X	X	X				X
Bakeware	713C05		Terracotta brown dish (cassolette)	20	11.5	450			X		X	X					
Bakeware	713C06		Terracotta brown dish (cassolette)	20	14.5	400	X				X	X	X				
Bakeware	713C07		Terracotta brown dish (cassolette)	20	15.5	400				X	X	X					
Bakeware	713C08		Terracotta brown dish (cassolette)	20	11.5	180		X			X	X	X				
Bakeware	713C12		Terracotta brown dish (cassolette)	17	11.5				X		X	X					
Bakeware	713C27		Terracotta brown oven dish (casserole)	24	41*29	3500				X	X		X				
Bakeware	916C16		Stoneware green dish (ramekin)	12	9.5	150				X	X						
Bakeware	916C17		Stoneware blue(ramekin)	12	9.5	150				X	X						
Bakeware	C6		Terracotta brown dish (cassolette)	12	14.5	200				X	X	X	X				
Bakeware	C14		Terracotta brown dish (cassolette)	12	11.5	150				X	X	X	X				
crystal	313G01		Lead crystal tumbler (PbO: 28 %)	50	9.5	180			X	X	X	X		X			X
crystal	313G02		Lead crystal plate (PbO: 28 %)	50	11.5	30	X			X	X	X		X			X
crystal	314G03		Lead crystal stem glass	48	6	420				X	X	X		X			X
crystal	314G04		Lead Crystal glass, green	30	5	75				X	x	x		x			x
crystal	314G05		Lead Crystal glass, amber	30	8	240				X	x	x		x			x
crystal	314G06		Lead Crystal glass, clear	30	6.5	240				X	x	x		x			x
crystal	314G07		Lead Crystal glass, red	30	6	110				X	x	x		x			x
crystal	314G08		Lead Crystal cup, gold decor	30	7.5	100 rim test 125 test holloware				X	x	x		x	x		x

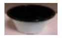
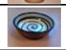
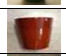
							tests done by				type of test comparisons performed						
Type	Anon. code	SAMPLE	Description	N° of items	Diameter [cm]	Simulant vol.[mL] (internal vol.)	NRLUK	NRL DE	NRL BE	JRC	acetic acid 4%	citric acid 0.5%	Tomato puree pH3.5	White wine	Rim (AA 4%; CA 0.5%)	Rim AA 4% Wax-no wax	Accel. test
crystal	414G01		Lead Crystal stem glass	30	7	600				X	X	X		X			X
crystal	513G01		Lead crystal goblet (PbO 40 %)	50	8.5	250				X	X	X		X			X
crystal	613G01		Lead crystal stem wine glass (PbO 24 %)	50	8.5	220			X	X	X	X		X			X
crystal	613G02		Lead crystal stem wine glass (PbO 24 %)	50	5	50	X	X		X	X	X		X			X
crystal	813G01		Lead crystal hollow plate	50	14.5	130		X		X	X	X		X			X
crystal	813G02		Lead crystal flute	47	5.5	200		X		X	X	X		X			X
crystal	814G03		Lead crystal tumbler	52	5.5	250				X	X	X		X			X
Flatware	213C02		Porcelain red plate with multicolour decoration	50	22	100	X			X	X	X					X
Flatware	213C08		Porcelain blue plate	50	18	270		X			X	X	X				
Flatware	213C11		Porcelain multicolour plate	50	16.5	250			X		X	X					
Flatware	413C02		Porcelain dessert plate with multicolour decoration	20	19	250			X		X	X					
Flatware	413C04		Porcelain decorated plate	20	19	110				X	X	X					X
Flatware	413C11		Porcelain decorated dessert plate	46	18.5	100			X	X	X	X					X
Flatware	413C13		Porcelain yellow coloured coffee plate	50	12	40	X	X	X	X	X	X					X
Flatware	413C15		Porcelain green coloured coffee plate	50	12	40	X	X	X	X	X	X					X
Flatware	413C17		Porcelain red coloured coffee plate	50	12	40	X	X	X	X	X	X					X
Flatware	413C18		Porcelain blue coloured flat plate	50	20	100	X	X	X	X	X	X	X				

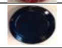
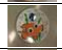
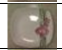
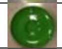
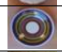
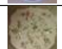
							tests done by				type of test comparisons performed						
Type	Anon. code	SAMPLE	Description	N° of items	Diameter [cm]	Simulant vol.[mL] (internal vol.)	NRLUK	NRL DE	NRL BE	JRC	acetic acid 4%	citric acid 0.5%	Tomato puree pH3.5	White wine	Rim (AA 4%; CA 0.5%)	Rim AA 4% Wax-no wax	Accel. test
Flatware	413C21		Porcelain pink coloured coffee plate	50	11	40				X	X	X					X
Flatware	413C22		Porcelain purple coloured coffee plate	50	11	40				X	X	X					X
Flatware	413C26		Porcelain decorated serving plate	30	30	250				X	X	X					X
Flatware	413C27		Porcelain decorated plate	30	23.5	250				X	X	X					X
Flatware	615C12		Porcelain plate decorated with coloured fruits	6	21	300				X	X						
Flatware	615C14		Porcelain plate decorated in blue and silver	6	22	300				X	X						
Flatware	615C16		Porcelain green plate decorated with blue flowers	6	26.5	500				X	X						
Flatware	615C20		Porcelain blue plate decorated with white flowers	6	21	250				X	X						
Flatware	713C09		Earthenware Multicolour plate	20	18.5	150				X	X	X	X				X
Flatware	713C17		Porcelain decorated plate with black designs	50	10	50	X	X		X	X	X					
Flatware	713C18		Porcelain decorated plate with blue designs	50	10	50			X	X	X	X					
Flatware	713C19		Porcelain decorated plate with brown designs	50	10	50		X	X		X	X					
Flatware	713C20		Earthenware multicolour plate	20	28	250				X	X	X					X
Flatware	713C22		Multicolour plate	20	14.5	70				X	X	X					X
Flatware	913C02		Fine bone china multicolour plate	50	23.5	100		X		X	X	X					X
Flatware	913C05		Fine Earthenware decorated plate with blue Dutch-type design	48	19.3	140		X		X	X	X					X
Holloware	113C01		Porcelain-enameled metal soup plate	50	20.5	450				X	X	X					

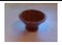
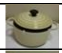
							tests done by				type of test comparisons performed						
Type	Anon. code	SAMPLE	Description	N° of items	Diameter [cm]	Simulant vol.[mL] (internal vol.)	NRLUK	NRL DE	NRL BE	JRC	acetic acid 4%	citric acid 0.5%	Tomato puree pH3.5	White wine	Rim (AA 4%; CA 0.5%)	Rim AA 4% Wax-no wax	Accel. test
Holloware	113C02		Porcelain-enameled metal measuring jug	50	10	1100			X		X	X					
Holloware	113C03		Porcelain-enameled metal mug	50	8.5	220		X		X	X	X					
Holloware	213C07		Porcelain blue coloured cup	50	8	300		X			X	X					
Holloware	213C09		Porcelain blue coloured bowl	50	14.5	430	X				X	X					
Holloware	413C06		Ceramic red coloured cup	20	8	240		X			X	X					
Holloware	615C13		Porcelain soup plate decorated (fruits)	6	23	500				X	X						
Holloware	615C15		Porcelain soup plate decorated	6	23	500				X	X						
Holloware	615C17		Porcelain soup green plate decorated with blue flowers	6	23	500				X	X						
Holloware	615C18		Porcelain green serving platter decorated with blue flowers	6	34*26	1000				X	X						
Holloware	615C19		Porcelain soup blue plate decorated with white flowers	6	23	500				X	X						
Holloware	713C01		Brown terracotta pot	20	7.5	250				X	X	X	X				X
Holloware	713C03		Terracotta plate decroated with spiral	20	14	350			X		X	X					
Holloware	713C04		Terracotta yellow coloured bowl	20					X		X	X					
Holloware	713C11		Terracotta brown cup	25	7.5	240	X				X	X					
Holloware	713C21		Erthenware yellow mortar	24	6.5	75				X	X						
Holloware	713C23		Terracotta brown bowl	38	12.5	150				X	X	X					X
Holloware	713C24		Terracotta blue cazuela	36	19	700				X	X		X				
Holloware	713C25		Terracotta green cazuela	36	20	700				X	X		X				

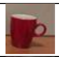
							tests done by				type of test comparisons performed						
Type	Anon. code	SAMPLE	Description	N° of items	Diameter [cm]	Simulant vol.[mL] (internal vol.)	NRLUK	NRL DE	NRL BE	JRC	acetic acid 4%	citric acid 0.5%	Tomato puree pH3.5	White wine	Rim (AA 4%; CA 0.5%)	Rim AA 4% Wax-no wax	Accel. test
Holloware	713C28		Terracotta green pot/cup	20	7	100				X	X	X					X
Holloware	713C30		Terracotta brown pot/cup	24	7.5	180				X	X						
Holloware	913C03		Stoneware Light blue coloured plate	50	22	250			X	X	X	X					
Holloware	913C08		Stoneware jug with handle	50	8	250			X	X	X	X					
Holloware	913C09		Stoneware jug without handle	50	7	200				X	X	X					
Rim	213C01		Porcelain cappuccino cup decorated	50	8.5	140 rim test (200)				X					X		
Rim	213C03		Porcelain cup decorated outside	50	8	90 rim test (260)				X					X		
Rim	213C10		Ceramic mug decorated outside	24	8	140 rim test (300)				X					X		
rim	413C03		Porcelain coffee cup decorated outside ;	20	9	130 rim test (250)				X					X		
rim	413C10		Porcelain coffee cup decorated outside	46	6.5	140 rim test (65)				X					X	X	
rim	413C12		Porcelain yellow coffee cup	50	5	100 rim test (75)		X		X					X	X	
rim	413C14		Porcelain green coffee cup	50	5	100 rim test (75)		X		X					X	X	
rim	413C16		Porcelain red coffee cup	50	5	100 rim test (75)		X		X					X	X	
rim	613C09		Porcelain colour coffee cup	12	5.5	100 rim test (55)				X					X		

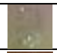
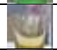
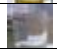
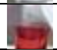
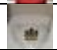
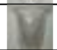
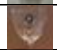
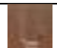
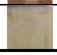
Annex 2 – all results

			Li	Al	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Cd	Sn	Ba	Pb
DSV [µg/kg]	M		600	1000		1200	100	100	2500	84	72	1000	1500	18	10	5	50000	1000	10
Sample Id			HOLLOWARE I /III MIGRATION ACETIC ACID 4 % [µg/kg]																
113C01	I		135.15		257.38	1.98	0.39	0.84	183.06	7.02	0.51	23.97	<LOD	0.31	0.38	0.07	<LOD	6.69	0.99
	III		17.90		188.89	0.27	<LOD	<LOD	23.04	0.99	<LOD	2.56	<LOD	<LOD	0.05	<LOD	1.28	1.09	<LOD
113C02	I		13.14	465.95		1.09	0.37		19.91	1.71	0.04	4.39	<LOD		0.46		1.92	44.62	1.31
	III		4.04	144.55		0.55	<LOD	1.98	152.65	1.21	0.39	1.25	<LOD	<LOD	0.91	<LOD	<LOD	6.56	0.69
113C03	I		94.83		103.80	2.22	11.25	291.89	202.01	53.26	98.03	135.63	<LOD		1.95	1.45	0.55	340.26	<LOD
	III		13.50		40.66	0.36	2.08	47.30	48.50	8.65	11.37	18.22	<LOD	<LOD	0.33	0.17	0.89	55.76	<LOD
213C07	I		0.08	50.36	-	0.02	0.78	1.15	5.14	7.63	0.21	0.49	4.51	0.02	0.23	0.01	0.81	0.93	0.58
	III		0.03	36.82	-	0.01	0.93	1.50	10.62	0.62	0.24	<LOD	3.80	0.02	0.22	0.01	0.38	1.35	0.31
213C09	I		<LOD	29.29	<LOD	0.16	<LOD	<LOD	<LOD	8.90	<LOD	2.88	5.42	<LOD	<LOD	<LOD	1.28	<LOD	<LOD
	III		<LOD	4.55	2.31	<LOD	<LOD	<LOD	<LOD	0.39	<LOD	1.97	2.47	<LOD	<LOD	<LOD	0.32	<LOD	<LOD
413C06	I		0.12	44.19	-	0.02	0.85	2.45	54.98	0.01	0.18	0.30	7.18	0.06	0.17	0.07	0.50	5.63	0.80
	III		0.39	41.64	-	4.74	10.89	28.16	880.06	0.01	16.35	97.02	167.55	17.34	0.24	41.93	33.67	1.92	4.10
615C13	I			83.16		0.20	1.97	<LOD	24.60	154.76		0.81	291.32			6.75		2.48	216.58
	III			19.42		<LOD	0.44	<LOD	4.70	17.09		<LOD	26.33			2.80		1.03	78.02
615C15	I			65.79		0.78	0.63	0.59	27.61	2196.10		5.38	3578.33			0.57		0.92	230.90
	III			8.54		0.24	1.49	<LOD	6.25	91.81		3.30	148.04			0.04		0.13	39.28
615C17	I			379.95		0.69	0.76	0.38	26.62	612.90		2.17	411.98			0.02		3.48	483.86
	III			64.61		<LOD	0.14	<LOD	7.48	108.65		<LOD	68.52			<LOD		0.48	87.19
615C18	I			176.72		1.38	0.40	<LOD	7.78	316.83		0.49	210.52			0.06		1.90	317.86
	III			27.48		<LOD	0.13	<LOD	<LOD	80.86		<LOD	36.51			<LOD		1.07	55.04
615C19	I			1099.57		0.56	0.46	1.02	116.21	617.66		7.70	794.41			0.39		228.73	707.63
	III			326.65		<LOD	0.13	0.25	34.75	183.96		0.99	238.21			0.11		53.17	195.15
713C01	I			288.64		1.49	0.31	8.51						0.56		0.53		8.11	347.50
	III			246.44		2.30	0.15	15.63				<LOD	<LOD	1.31		0.29		13.63	41.40
713C03	I		0.08	15.80				0.14	23.56	1.86	6.07	0.24	3.97					0.65	211.58
	III		<LOD	<LOD		<LOD	<LOD	<LOD	<LOD	0.18	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	13.91
713C04	I		1.15	5229.22		1.64		3.65	147.74	0.26	2.01			0.39				6.93	243.72
	III		3.94	2643.62		1.44	<LOD	11.38	167.11	0.52	4.59	0.34	<LOD	0.63	<LOD	<LOD	<LOD	7.02	53.79
713C11	I		1.82	822.22	6.35	0.95	<LOD	8.34	138.81	0.34	<LOD	2.77	6.70	0.76	0.15	<LOD	<LOD	10.58	466.36
	III		3.06	655.03	3.15	1.29	<LOD	12.72	120.70	0.53	<LOD	0.84	8.60	1.11	0.27	<LOD	<LOD	9.70	335.19
713C21	I		<LOD	65.84	0.27	0.11	40.87	0.24	74.47	0.11	<LOD	0.20	<LOD	0.33		0.01	1.28	2.20	11.22
	III		<LOD	0.71	<LOD	0.04	40.53	<LOD	69.70	<LOD	<LOD	0.68	<LOD	0.20		0.03	0.99	0.59	1.10
713C23	I		<LOD	116.68	<LOD	<LOD	<LOD	0.41	<LOD	0.01	<LOD	5.16		<LOD		<LOD		6.30	75.65
	III			84.16	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1.06				<LOD		9.50	7.74
713C24	I		<LOD	12929.11	10.67	71.17	2.06	81.88	1581.63	354.92	<LOD	4.94	224.02	26.32	<LOD	<LOD	20.06	247.34	1583.75
	III		<LOD	10967.43	9.39	119.77	1.94	106.65	1192.00	198.49	<LOD	4.98	165.02	31.77	<LOD	<LOD	0.73	155.56	881.89
713C25	I		<LOD	21306.78	13.31	121.41	8.10	207.12	2389.10	4.81	<LOD	7.41	923.54	33.31	<LOD	<LOD	<LOD	138.85	495.13
	III		<LOD	12406.45	7.79	113.11	3.49	225.21	1223.82	2.74	<LOD	5.61	378.71	29.06	<LOD	<LOD	<LOD	74.14	191.09
713C28	I		39.15	2418.82	147.89	23.36	5.78	37.33	586.91	<LOD	0.42	5512.22	3167.56	11.23		1.67	2.22	227.45	19061.17
	III		25.52	1053.81	79.57	23.13	2.81	58.38	106.54	2.32	0.54	611.76	204.29	10.40		0.23	4.00	36.89	2332.85
713C30	I		13.16	3891.77	5.13	11.93	<LOD	77.80	<LOD	2.20	4.10	0.67	13.70	3.99		0.45	<LOD	16.92	321.89
	III		8.94	906.18	0.90	2.74	<LOD	62.42	<LOD	1.02	2.26	<LOD	<LOD	1.20		0.25	<LOD	6.94	76.38
913C03	I		0.19	63.05	0.63	0.25	<LOD	0.60	<LOD	0.17	<LOD	3.39	108.71	0.03		<LOD	<LOD	6.01	0.40
	III		<LOD	6.90	0.37	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	<LOD		<LOD	<LOD	0.55	<LOD
913C08	I		0.96	18.92	0.22	<LOD	0.12	<LOD	<LOD	<LOD	<LOD	0.73	10.61	0.02		0.01	0.62	0.16	0.33
	III		0.11	1.83	0.36	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	<LOD		<LOD	<LOD	0.14	<LOD
913C09	I		1.74	20.58	0.20	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.37	8.93	0.01		0.01	0.58	0.20	0.52
	III		0.22	3.38	0.38	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	<LOD		<LOD	<LOD	0.06	<LOD

			Li	Al	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Sn	Sb	Ba	Pb
DSV [µg/dm²]	M		120	200		240	20	20	500	17	14	200	300	4	1	10000		200	2
Sample Id									FLATWARE I / III MIGRATION ACETIC ACID 4 % [µg/dm²]										
213C02	I		0.005	3.72	0.04	0.01	0.01	0.05	0.25	0.03	0.002	0.02	0.23		0.003	0.04	0.002	0.03	0.07
	III		<LOD	0.34	0.004	<LOD	<LOD	<LOD	<LOD	0.002	<LOD	0.01	<LOD		<LOD	0.031	<LOD	0.004	<LOD
213C08	I		0.03	10.40	-	0.18	0.18	0.49	3.01	5.52	<LOD	0.88	1.56	0.53	0.01	0.32	0.04	0.54	0.42
	III		0.01	9.32	-	0.01	0.18	0.29	3.48	0.09	0.030	0.18	1.07	0.02	0.01	0.22	0.02	0.30	0.26
213C11	I			2.72					0.37	0.08					<LOD	0.34	0.17	<LOD	<LOD
	III		0.01	3.97		0.04	0.03	<LOD	0.48	<LOD	0.03	0.03	0.51	0.12	<LOD	0.39	0.56	<LOD	0.21
413C02	I		0.74	40.99			0.11	0.23	3.02	5.01	0.08	0.09	13.03	0.05	11.73	0.23	0.09	4.05	181.65
	III		0.26	12.56		0.06	0.04	0.09	0.97	2.07	0.09	<LOD	4.48	0.05	3.70	0.18	0.15	0.94	72.30
413C04	I		0.04	6.52	0.04	0.01	0.13	0.03	0.60	0.07	0.02	0.07	0.99	0.05	0.02	0.04	0.02	0.13	12.53
	III		0.01	0.63	0.02	<LOD	0.006	0.01	0.01	0.005	<LOD	0.005		0.01	<LOD	0.03	0.005	0.03	2.01
413C11	I		0.02		0.18	0.03	0.01	1.67	1.34	5.39	0.06	0.06	0.41		0.007	0.03		0.15	7.12
	III		0.003		<LOD	<LOD	0.01	0.18	0.04	1.05	0.008	<LOD	<LOD		<LOD	0.16		0.02	0.61
413C13	I		0.03	3.80	0.04	0.003	0.01	0.01	0.24	0.001	0.01	0.01	0.08	0.003	0.001	0.06	0.03	0.05	0.08
	III		0.11	4.67	0.21	<LOD	0.006	0.02	0.33	<LOD	0.014	0.026		0.002	0.001	0.15	<LOD	2.05	0.09
413C15	I		1.21	21.29	0.27	0.06	0.04	0.06	1.51	0.30	0.13	0.11	6.81	0.05	15.44	0.41	0.04	0.50	111.29
	III		0.32	4.25	0.07	0.03	0.02	0.01	0.47	<LOD	<LOD	<LOD		0.03	3.66	0.57	<LOD	<LOD	25.93
413C17	I		1.09	38.50	1.03	0.02	0.03	0.08	1.77	0.01	0.10	0.31	9.49	0.02	38.68	0.19	0.03	51.66	150.37
	III		0.16	4.31	0.26	0.008	0.01	<LOD	0.17	<LOD	<LOD	<LOD		0.01	7.30	0.10	<LOD	3.91	26.19
413C18	I			8.40				0.01	0.07	0.88	0.01	0.26			0.003			0.21	11.60
	III			3.39			<LOD	<LOD	<LOD	0.06	<LOD	<LOD			<LOD			0.13	0.71
413C21	I		0.32	20.68	0.07	0.01	<LOD	0.02	0.81	0.01	0.01	0.35	24.28	0.004	0.03	0.10	0.01	0.35	155.52
	III		0.12	4.77	-	0.01	<LOD	<LOD	0.24	<LOD	<LOD	<LOD	-	0.007	<LOD	0.16	<LOD	-	50.36
413C22	I		0.33	3.75	0.10	0.004		0.03	0.33	0.002	0.01	0.09	5.14	0.002	0.70	0.13	0.003	0.08	63.83
	III		0.06	0.12	<LOD	<LOD	<LOD	<LOD	1.02	<LOD	<LOD	<LOD	<LOD	0.004	0.10	0.08	<LOD	<LOD	9.31
413C26	I		0.46	29.61	0.59	0.01	0.47	0.03	1.02	0.27	0.08	0.55	1.91		0.02	0.01		4.17	3.46
	III		0.18	6.76	0.19	<LOD	0.06	0.008	0.19	0.30	0.11	0.18	0.68		0.005	<LOD		2.15	1.20
413C27	I		1.68	77.87	0.36	0.02	0.25	0.07	1.31	0.05	0.02	0.36	3.65		0.01	0.12	0.03	6.54	6.36
	III		0.51	30.90	0.06	<LOD	0.05	0.02	0.35	0.006	<LOD	0.11	1.62		0.003	0.039	0.0027	4.20	1.74
615C12	I			12.94		0.16	0.30	0.03	3.15	34.01		0.27	63.67		1.85			0.51	48.08
	III			2.97		0.01	0.05	<LOD	0.99	2.33		0.02	3.52		0.45			0.14	12.88
615C14	I			14.21		0.06	0.13	0.20	4.96	795.21		1.82	1325.30		0.19			0.16	80.84
	III]			2.32		0.01	0.03	<LOD	0.46	6.62		0.02	9.63		0.01			0.03	11.14
615C16	I			102.37		0.10	0.17	0.09	5.52	173.22		0.64	123.38		0.02			1.09	188.79
	III			21.36		0.01	0.04	0.005	1.14	40.30		0.07	24.55		0.004			0.22	39.22
615C20	I			131.70		0.14	0.10	0.11	12.81	55.43		1.18	72.17		0.67			0.62	135.48
	III			40.26		0.04	0.02	0.03	4.01	17.29		0.16	22.37		0.18			0.18	39.63
713C09	I			132.77			0.03	1.16	16.05	0.08	0.02	<LOD			0.02			0.59	40.95
	III			60.42			0.03	1.32	5.39	0.03	0.02	<LOD			0.01			0.48	6.46
713C17	I			1.20			0.02	0.06	0.11	1.97	0.62	0.16			<LOD			0.36	0.06
	III			<LOD			<LOD	0.02	0.19	0.45	0.18	0.34			<LOD			0.33	<LOD
713C18	I			5.25			0.02		0.06	0.16	0.01	<LOD			<LOD			0.40	0.03
	III			3.37			<LOD	<LOD	<LOD	0.02	0.004	<LOD			<LOD	<LOD	<LOD	0.28	<LOD
713C19	I		0.01	6.28		0.12		0.03	2.07	0.10		0.32	0.86	0.54	0.05	0.12	0.04	0.03	0.30
	III		<LOD	0.51		0.01	<LOD	<LOD	0.80	0.01	<LOD	0.03	<LOD	0.01	<LOD	<LOD	<LOD	<LOD	0.03
713C20	I		0.005	1.43	0.03	0.001	0.01	0.01	0.05	0.74	0.003	0.02	0.12	0.003	0.0002	0.01	0.01	0.06	20.96
	III		0.002	0.22	0.02	<LOD	<LOD	<LOD	<LOD	0.89	<LOD	0.01		<LOD	<LOD	<LOD	0.001	0.03	2.58
713C22	I		0.01	1.15	0.02	0.001	0.003	0.003	0.01	0.004	0.0004	<LOD	0.56	0.001	0.02	0.03	0.001	0.06	0.73
	III		0.01	0.50	0.02	<LOD	<LOD	0.02	0.07	0.01	<LOD	0.01		<LOD	0.01	<LOD	<LOD	0.03	0.19
913C02	I		0.12	2.97	0.03	0.001	0.03	0.01	0.08	0.11	0.01	0.03	0.33	0.001	0.09	0.002	0.004	0.87	1.79
	III		0.02	0.75	0.01	<LOD	0.003	<LOD	<LOD	0.004	<LOD	0.01		<LOD	0.01	<LOD	<LOD	0.05	0.26
913C05	I		0.13	2.87	0.01	0.003	0.002	0.01	0.01	0.04	0.001	0.03	0.73		<LOD	0.07	0.004	3.86	0.20
	III		0.02	0.41	<LOD	<LOD	<LOD	<LOD	<LOD	0.005	<LOD	0.006	<LOD		<LOD	0.02	0.0006	3.24	0.02

			Li	Al	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Cd	Sn	Ba	Pb
DSV [µg/kg]																1.9			3.8
Sample Id	M								**BAKEWARE**	I/III MIGRATION ACETIC ACID 4 % [µg/kg]									
C6	I				1.67			36.04	258.89	0.29		14.23	<LOD			0.12		100.98	1583.32
	III				22.72			51.80	1400.62	0.34		9.53	<LOD			0.12		173.70	1203.32
C14	I		98.26	17928.72	13.04		16.46	368.07		5.96		18.02		99.25		0.06		271.70	27.02
	III		82.60	10714.46	7.31		7.29	498.93		4.79		13.06		120.28		0.05		555.75	14.95
416C28	I		-	282.62	-	-	-	3.28	21.28	<LOD	-	4.75	84.88	-	-	308.98	-	5.76	1029.87
	III		-	83.78	-	-	-	0.52	<LOD	<LOD	-	0.50	23.30	-	-	75.16	-	1.07	254.65
416C29	I		-	12.74	-	-	-	<LOD	4.71	0.47	-	0.73	<LOD	-	-	<LOD	-	0.12	0.61
	III		-	<LOD	-	-	-	<LOD	<LOD	<LOD	-	<LOD	<LOD	-	-	<LOD	-	<LOD	<LOD
416C30	I		-	58.57	-	-	-	<LOD	4.48	67.06	-	1.17	<LOD	-	-	0.21	-	5.99	83.90
	III		-	6.39	-	-	-	<LOD	<LOD	5.30	-	0.27	<LOD	-	-	<LOD	-	0.79	7.06
416C31	I		-	31.25	-	-	-	<LOD	17.69	<LOD	-	2.38	20.40	-	-	0.07	-	1.78	17.41
	III		-	6.22	-	-	-	<LOD	<LOD	<LOD	-	0.24	<LOD	-	-	<LOD	-	0.31	1.63
713C02	I			40197.50		32.93	21.83	525.88			9.24	19.00	95.36	17.95		0.10		65.50	764.39
	III			10963.54		7.85	4.72	265.44			2.90	5.39	40.10	9.33		0.05		55.20	152.33
713C05	I		6.03	2839.44		1.45		13.19	74.64	0.26	3.66	2.00	1378.73	7.18				457.84	7.39
	III		2.77	1647.37		0.56	<LOD	12.71	44.22	0.16	2.10	0.28	64.95	1.12	<LOD	<LOD	<LOD	133.80	1.67
713C07	I		<LOD	79.17		42.00	1.77	61.33		<LOD	1.40	2.70	56.37	12.04		<LOD		31.93	1.06
	III			52.21		25.97	1.56	96.42			0.88	1.11	20.94	13.07		<LOD		76.92	<LOD
713C08	I		28.29	833.73	-	17.23	8.35	44.24	252.24	1.23	1.18	24.80	95.18	5.21	2.34	11.49	17.31	75.18	2973.80
	III		28.44	616.33	-	13.74	8.21	128.93	95.77	1.91	2.71	38.41	135.97	4.68	5.38	0.08	81.66	216.07	586.32
713C12	I		9.42	11041.89		20.44		21.47	6.35	0.13		0.81		1.01				43.38	489.84
	III		13.69	687.01		25.03	<LOD	52.98	<LOD	0.49	<LOD	1.64	<LOD	0.64	<LOD	<LOD	<LOD	56.06	106.38
713C15	I		8.83	533.90		0.32		2.37	235.56	0.06		1020.61	15.47	0.67		0.67		102.81	11034.90
	III		1.68	117.10		<LOD	<LOD	0.54	58.89	<LOD	<LOD	155.20	<LOD	0.16	<LOD	0.14	<LOD	19.80	2498.33
713C16	I		<LOD	285.13	<LOD		8.94	1.76	21.93		2.05	1.00	27.51	<LOD		0.02		19.60	1244.85
	III			463.70	<LOD		5.99	2.30	31.64		0.79	<LOD	<LOD			<LOD		13.14	197.02
713C27	I		<LOD	14672.17	28.83	48.94	20.02	92.44	2859.78	1.98	<LOD	15.21	780.10	15.77	<LOD	<LOD	2.49	192.23	3664.29
	III		<LOD	8475.15	24.88	60.77	8.73	66.52	1359.21	2.87	<LOD	10.64	311.24	13.79	<LOD	<LOD	1.64	79.23	1615.44
916C16	I		-	355.40	399.58	-	0.60	90.97	126.67	76.37	0.23	1488.69	1711.36	-	-	1.52	-	32.53	0.77
	III		-	5.44	20.11	-	<LOD	1.02	3.90	0.76	<LOD	6.61	13.95	-	-	0.02	-	0.17	<LOD
916C17	I		-	93.23	193.14	-	0.20	31.14	31.80	63.17	<LOD	6.09	482.62	-	-	0.14	-	1.31	<LOD
	III		-	6.90	9.18	-	<LOD	1.12	23.28	2.05	<LOD	<LOD	20.97	-	-	<LOD	-	0.43	<LOD
1015C01	I		-	250.87	-	<LOD	0.75	0.60	7.22	<LOD	-	0.98	43.97	-	-	<LOD	-	39.82	1.67
	III		-	203.61	-	<LOD	<LOD	-	<LOD	<LOD	-	0.26	19.63	-	-	<LOD	-	22.75	<LOD
1016C02	I		-	1717.32	192.92	-	4.65	326.65	55561.61	5.46	8.24	7.93	19.25	-	-	1.67	-	49.90	42.00
	III		-	779.67	59.56	-	14.19	-	115901.44	3.37	6.66	3.19	9.62	-	-	0.51	-	23.10	<LOD
1016C03	I		-	810.88	120.89	-	0.54	10.79	676.34	2.42	0.70	31.54	7.48	-	-	0.02	-	20.35	0.51
	III		-	107.72	44.35	-	<LOD	-	34.57	0.28	<LOD	0.48	<LOD	-	-	<LOD	-	0.51	<LOD
1016C04	I		-	40.31	7.24	-	1.11	16.90	25.47	9.00	<LOD	12.39	<LOD	-	-	<LOD	-	11.22	<LOD
	III		-	3.09	1.59	-	0.18	1.84	3.09	1.00	<LOD	1.37	<LOD	-	-	<LOD	-	1.35	<LOD

			Li	Al	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Zr	As	Cd	Sb	Ba	Pb
DSV [µg/kg]																			
Sample Id									RIM	I/III MIGRATION ACETIC ACID 4 % [µg/L]									
DE13C03	I		-	51.02		0.66	2.25	<LOD	58.70	1.95	-	0.49	11.77			0.13		1.12	116.37
	III		-	8.77		<LOD	0.11	<LOD	<LOD	0.23	-	<LOD	<LOD			0.01		0.21	27.86
DE13C10	I		<LOD	75.50		0.24	<LOD	20.56	147.82	104.80	3.51	13.06	165.30		0.86	0.28		7.46	109.44
	III		<LOD	21.41		<LOD	<LOD	3.07	15.40	47.36	0.44	1.22	1072.21		<LOD	0.12		16.02	8.70
DE13C12	I		<LOD	16.50		<LOD	<LOD	1.08	25.13	<LOD	1.54	7.95	88.67		0.39	0.10		4.41	2.08
	III		<LOD	15.43		<LOD	<LOD	0.32	8.23	0.31	<LOD	1.12	667.96			0.07		0.85	0.88
DE13C14	I		4.03	98.50		<LOD	1.84	1.31	66.19	1.15	0.79	9.38	72.78		0.25	52.13		3.77	374.03
	III		0.22	25.50		<LOD	<LOD	0.41	19.19	0.56	<LOD	0.78	667.01		<LOD	12.70		1.41	71.96
DE13C16	I		11.34	237.23		<LOD	0.47	1.37	73.67	<LOD	1.64	7.46	142.08		0.50	607.71		352.05	905.57
	III		0.14	31.89		<LOD	<LOD	0.32	10.07	0.34	0.30	1.68	670.30		<LOD	134.78		25.82	120.23
FI13C01	I		<LOD	12.29		0.50	<LOD	0.40	11.71	1.60	0.88	2.83	48.81		0.36	0.04		5.32	6.51
	III		<LOD	5.95		0.27	<LOD	<LOD	<LOD	0.37	0.24	0.41	348.89		0.10	0.03		0.30	<LOD
FI13C03	I		0.11	6.70		<LOD	<LOD	0.31	6.87	0.43	0.38	0.90	22.75		0.12	0.05		1.81	0.29
	III		<LOD	3.32		<LOD	<LOD	<LOD	<LOD	0.25	<LOD	0.51	174.61		<LOD	0.03		0.29	<LOD
FI13C10	I		<LOD	22.07		<LOD	<LOD	0.39	8.07	0.16	0.69	1.49	37.63		0.16	0.01		1.60	0.68
	III		<LOD	2.10		<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	22.54		<LOD	<LOD		0.10	<LOD
IT13C09	I		<LOD	43.50		<LOD	<LOD	1.29	35.76	2.76	1.03	3.86	55.03		0.19	0.71		1.96	66.18
	III		<LOD	20.25		<LOD	<LOD	0.49	13.10	<LOD	<LOD	1.02	1096.77		<LOD	0.20		0.88	5.36
FR14G08	I			196.42	39.00		0.12	0.27	22.59				27.23	9.96		189.86	2.71	1.40	17954.27
	III			5.78	0.86		<LOD	<LOD	<LOD				<LOD	0.22		0.09	0.16	0.11	57.87

			Al	Ti	Cr	Mn	Fe	Zn	As	Zr	Ag	Sb	Cd	Sn	Ba	Pb
DSV [µg/kg]			1000		100	400	2500	1500	18		50	40	5	50000	1000	10
Sample Id	M						CRYSTAL WARE		I/III MIGRATION ACETIC ACID 4% [µg/kg]							
DE13G01	I															119.47
	III															12.70
FR13G01	I							0.105			<LOD	1.15			0.48	421.15
	III]											0.16			1.33	100.72
FR13G02	I							13.91			<LOD	8.26			0.36	1273.57
	III							<LOD			<LOD	0.67			0.07	280.07
FR14G03	I											1.02				158.03
	III											0.08				31.08
FR14G04	I		4.27	0.13	0.22		3.72	61.58	0.65	0.50		4.27		0.40	2.34	821.83
	III		2.01	<LOD	<LOD		<LOD	<LOD	<LOD	<LOD		0.79		<LOD	0.30	178.97
FR14G05	I		3.34	0.12	0.01	0.08	1.03	22.93	0.10	0.09		1.91	0.006	0.04	1.65	648.49
	III		2.07	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD		0.30	<LOD	<LOD	0.26	98.49
FR14G06	I		3.50	0.11		0.05	0.89	21.55	0.11	0.05		3.29	0.005	0.05	2.53	572.84
	III		2.21	0.10	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD		0.57	<LOD	<LOD	0.40	120.38
FR14G07	I		6.44	0.15	0.69	0.30	5.03	21.93	4.16	0.54		3.56	0.053	0.38	0.90	1626.38
	III		1.81	<LOD	<LOD	<LOD	<LOD	<LOD	0.21	<LOD		0.18	<LOD	<LOD	<LOD	415.35
FR14G08	I		4.42	0.14				3.25		0.03		0.53	0.008	0.02	0.09	184.58
	III		2.73	<LOD				<LOD		<LOD		0.06	<LOD	<LOD	<LOD	20.33
IE13G01	I							<LOD			<LOD	<LOD			<LOD	263.62
	III							<LOD			<LOD	<LOD			<LOD	122.37
IT13G01	I							10.50			<LOD	0.93			0.79	382.72
	III							<LOD			<LOD	0.15			0.09	41.61
IT13G02	I							42.50			<LOD	1.60			14.71	718.26
	III							<LOD			<LOD	0.11			0.09	64.35
SL13G01	I							465.50			0.52	4.95			13.42	1868.31
	III							423.94			<LOD	0.86			2.17	187.65
SL13G02	I							42.71			<LOD	1.54			14.51	731.15
	III							<LOD			<LOD	0.17			3.39	114.84
SL14G03	I											0.38			4.96	177.03
	III											<LOD			0.68	19.54

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