



Report of the interlaboratory comparison organised by the European Reference Laboratory for Food Contact Material

ILC01 2011- Formaldehyde in food contact migration solution

G. Beldi, N. Jakubowska, M. Derda and C. Simoneau



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EC-JRC-IHCP

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G. Beldi, N. Jakubowska, M. Derda and C. Simoneau

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1. Summary

The Institute for Health and Consumer Protection (IHCP) of the European Commission's Directorate-General Joint Research Centre hosts the EU Reference Laboratory for Food Contact Materials (EURL-FCM). One of its core tasks is to organise interlaboratory comparisons (ILCs) among appointed National Reference Laboratories (NRLs).

This report presents the results of an ILC of the EURL-FCM which focused on the quantification of formaldehyde in migration solutions of 3% acetic acid from food contact materials. The test material used for the preparation of the migration solutions were melamine kitchenware (spoons) containing formaldehyde. The EURL prepared and distributed three concentration levels of migration solution. The general aim of the exercise was to assess the proficiency of the official control laboratories and consequently the participants were free to use any analytical method of their choice. However, in view of the support to Regulation 284/2011, EURL suggested to limit the methods to the two procedures included in EN 13130-23 (i.e. standard for food contact).

There were 62 participants to whom samples were dispatched (27 NRLs + 35 national control laboratories from Germany, Italy, United Kingdom, Poland, Spain, France, Portugal and Switzerland) and 61 participants which submitted results. The homogeneity and stability studies were performed by the EURL-FCM laboratory. The assigned values were obtained after applying the robust statistics to the results of the participants. Participants were invited to report 4 results for each concentration level. Laboratory results were processed using several algorithms: ISO 13528 [1], Harmonized protocol [8], DIN 38402 A45 (Q-Hampel) [5] and ISO GUIDE 35:2006 [11]. Standard deviations for proficiency assessment (also called target standard deviations) were set based on Horwitz equation [2].

As a conclusion of the ILC exercise on the quantification of formaldehyde in a migration solution of kitchenware in 3% acetic acid, this ILC showed that:

- The participation in the ILC was satisfactory regarding the number of the participating laboratories. Sixty one participants laboratories submitted their results. Six of the participants submitted results obtained using two different methods. From the EURL-NRL network all 27 laboratories reported results.
- More than 85% of all reported results were properly estimated.
- The results of the NRL-FCM laboratories were all satisfactory
- For the network of national control laboratories only one laboratory did not send any results.
- The comparison of results from the two preparation methods in EN 13130-23 were not significantly different. Both methods were found interchangeable.

2. Introduction

ILC studies are an essential and very important element of laboratory quality assurance. They allow individual laboratories to compare their analytical results with those from other laboratories while providing them with objective standards to perform against.

One of the core duties of the EU Reference Laboratories is to organize interlaboratory comparisons, as stipulated in Regulation (EC) No 882/2004 of the European Parliament and the Council [4].

In accordance with the above requirements the EU Reference Laboratory for Food Contact Material (EURL-FCM) organized in 2011 for the fourth year interlaboratory comparison tests for the network of appointed National Reference Laboratories (NRLs).

The objectives of the interlaboratory comparison (ILC) tests for 2011 were discussed and agreed in the plenary meeting with all NRLs held in December 2010 in Ispra, Italy. One ILC was decided as formaldehyde from melamine kitchenware.

Formaldehyde (CAS 50-00-0) is combined with melamine to produce items, which may be intended to come into contact with foods. Typical food contact applications of melamine kitchenware are children mugs, bowls, cups, plates, spoons. In some cases, formaldehyde may migrate into food.

3. Scope

The scope of this ILC was to test the competence of the appointed NRLs to analyze formaldehyde in migration solutions of 3% acetic acid from melamine kitchenware.

The different concentration levels of migration solution were obtained by dilution.

The assessment of the measurement results was done based on requirements laid down in international standards and guidelines [1, 2, 5, 7, 8, 11]

4. Time frame

A questionnaire was sent to the NRL-FCM network in the beginning of 2011 as a preliminary step with the aim to help in organisation of the ILC01 2011. The aim was to create an overview on

- 1) the sample preparation methods used by NRLs
- 2) the experience of NRLs to perform analysis of formaldehyde in food/food simulant

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24 NRLs replied to the questionnaire. The answers are summarised in Annex 1.

The ILC01 2011 was launched in May 2011. Invitation letters were sent to the laboratories on 26th April 2011 (Annex 2). Laboratories were invited to fill in a letter of confirmation of their participation (Annex 3).

The samples were prepared at the end of April 2011. Homogeneity tests were run in the beginning of May. The results from homogeneity test were accepted as time zero for stability testing.

The samples were dispatched to participants on 20th May 2011, together with the letters accompanying the samples (Annex 4) and a format for the compilation of results (Annex 6). Electronic ProLab files, where the result should be inserted, were sent to the participants by e-mail on 23rd May 2011.

The participants were asked to fill in a confirmation of the receipt of the samples (Annex 5)

The deadline for reporting was 17th June 2011.

5. Test materials

5.1 Preparation

The preparation of the test materials was done by the EURL-FCM.

The migration solutions were obtained after migration experiment immersing melamine kitchenware, mainly different melamine spoons in 3% acetic acid for 2 h at 70°C. The three samples were obtained by dilution of the original migration solution in order to obtain more reliable evaluation of the precision and reproducibility for the concentration range under, around and above the permitted limit (15 mg/kg), where the decision should be made by the Competent Authorities (table 1).

Table 1. Test materials

Exercise	Name	Sample
ILC 01 2011	FORM01	1 bottle of 3% acetic acid migration solution at level 1
	FORM02	1 bottle of 3% acetic acid migration solution at level 2
	FORM03	1 bottle of 3% acetic acid migration solution at level 3

5.2 Homogeneity assessment

The samples were tested for homogeneity by the EURL.

Ten randomly selected test specimens for each sample (FORM01, FORM02, and

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FORM 03) were analyzed in duplicate for formaldehyde, using the CEN 13130-23 chromotropic acid method.

The homogeneity was evaluated by the ProLab Software [3] according to the IUPAC International Harmonized Protocol [8], F-test and to the method proposed in the ISO 13528 [1]. The results together with their statistical evaluation are given in Annex 7.

All test materials showed sufficient homogeneity for the target standard deviation.

5.3 Stability test

Randomly selected specimens for each sample (FORM01, FORM02, and FORM 03) were stored at 3 different temperature conditions (+5°C, room temperature, +40°C). The test samples were monitored for stability by the EURL by periodical determination of formaldehyde from the date of preparation and homogeneity assessment to the closing of the ILC01.

The stability was evaluated as described in the ISO GUIDE 35:2006 [11].

No significant trend was observed for the test samples at all temperature conditions (+5°C, RT and +40°C) for the time of the ILC (Annex 8).

5.4 Distribution

The sample kits were dispatched to the participants by the EURL-FCM on 20th May 2011. Each participant received a box containing:

- a) the test materials – 3 migration solution samples;
- b) the accompanying letters with instructions on samples handling, analysis and reporting of results (Annex 4);
- c) a form that had to be sent back after receipt of the samples to confirm their arrival (Annex 5);
- d) a form for reporting the results in non-electronic format (Annex 6).

6. Instructions to participants

Complete instructions were given to all participants in the letters that accompanied the samples (Annex 4).

Laboratories were asked to report 4 results for each concentration level. Participants were asked to follow their own procedures and to indicate their sample preparation method – CR-chromotropic acid, AA-acetyl acetone, 2,4DNPH-2,4 dinitrophenylhydrazine or other, and instrumental method of analysis – UV-VIS, HPLC-DAD, LC-MS or other. However, in view of the support to Regulation 284/2011, it was suggested to limit the methods to the two procedures included in CEN 13130-23 (CR – chromotropic acid, AA – acetyl

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acetone). The results had to be reported using the unit of measure indicated in the instruction letter.

The results were reported in a special form sent to the participant (Annex 6)

7. Assigned values

As described earlier, the test materials used for this exercise were migration solutions of kitchenware in 3% acetic acid, prepared by the EURL.

As the “true” values could not be known, the assigned values were obtained after applying the robust statistics to the participants’ test results using a ProLab software [3].

8. Target standard deviation

The value of target standard deviation (σ_p) determines the limits of satisfactory performance in ILC test. It should be set as a value that reflects best practice for the analysis in question. The standard deviation of the reproducibility found in the collaborative trials is generally considered as an appropriate indicator of the best agreement that can be obtained between laboratories. However, it is not applicable to all cases. In the absence of appropriate collaborative trial data, σ_p can be derived from the appropriate form of the modified Horwitz equation [2].

For all migration samples of this ILC01 2011 exercise the target standard deviation was set to the one calculated by the Horwitz formula.

9. Evaluation of results

9.1 General observations

There were sixty two participants from twenty-six countries to whom samples were dispatched. Participants were the 27 NRL laboratories (NRL Malta represented by NRL UK, Sweden and Romania without NRL represented) and several national control laboratories from Member States especially Germany, Italy, United Kingdom, Poland, Spain, France, Switzerland as guests. They all received the samples. The ILC was closed permanently on 17th of June for statistical interpretation.

Sixty one laboratories submitted their results. As requested, most of the laboratories reported four results for each concentration level.

From the EURL-NRL network all 27 laboratories reported results.

9.2. Statistical evaluation of results

9.2.1. Determination of the consensus value and standard deviation of the interlaboratory comparison

The statistical evaluation of the results was performed using the ProLab software [3] applying different algorithms for the determination of the consensus value and its standard deviation according to ISO 13528 [1], DIN 38402 A45 [5] and ISO/TS 20612 [6]. The three mostly used algorithms for robust statistic determination of the consensus value - Q-median, Q/Huber-estimator and Q/Hampel estimator - gave very close results. The choice was made on Hampel estimator (DIN 38402 A45) as one of the most robust necessary especially when many outliers are present.

9.2.2. Identification of modes using kernel density plotting

Kernel density plots were additionally used to identify multi-modality in the reported values' distributions.

Frequently analytical results from a collaborative study are not normally distributed or contain values from different populations giving rise to multiple distribution modes. These modes can be visualised by using Kernel density plots [9, 10]. Kernel density plots were computed by the ProLab software [3] from the analytical results by representing the individual numeric values each as a normalised Gaussian distribution centred on the respective analytical value. The sum of these normal distributions formed then the Kernel density distribution.

9.2.3. Scores and evaluation criteria

Individual laboratory performance was expressed in terms of z-scores (z) in accordance with ISO 13528 [1] and the International Harmonised Protocol [8]

$$z = \frac{(x_{lab} - X_{assigned})}{\sigma_p},$$

where

x_{lab}	is the measurement result reported by a participant
$X_{assigned}$	is the assigned value
σ_p	is the target standard deviation for proficiency assessment

The z- scores can be interpreted as follow:

$ z \leq 2$	satisfactory result
$2 < z \leq 3$	questionable result
$ z > 3$	unsatisfactory result

The z-scores compared the participants' deviation from the assigned value with target standard deviation accepted for the interlaboratory comparison σ_p .

9.3 Laboratory results and scores

Summary of the laboratories results are given in table 2 and figures 1-3.

They are presented with their reported sample preparation methods (CR, AA, 2-DNPH and other). Also shown are the robust repeatability standard deviations and robust reproducibility standard deviations calculated according to Q-Hampel algorithm (ISO 20612:2007 and DIN 38402 A45) by ProLab software as well as assigned values and target standard deviation of the ILC.

Table 2. Summary of results calculated according to DIN 38402 A45

	FORM01	FORM02	FORM03
Method DIN 38402 A45			
Robust Mean = Assigned value , mg/kg	6.78	15.91	26.72
Robust Repeatability s.d., mg/kg	0.09	0.19	0.27
Robust Reproducibility s.d., mg/kg	0.64	1.29	1.96
Rel. target s.d., %	11.99	10.55	9.76
Robust Rel. reproducibility s.d., %	9.51	8.12	7.34
lower limit of tolerance, mg/kg	5.15	12.55	21.51
upper limit of tolerance, mg/kg	8.40	19.26	31.94
No. of results	67	67	67

Figures 4-6 represent Kernel density plots with calculated limit of tolerance ($|z| \leq 2$) according to DIN 38402 A45.

Figures 7-9 present graphs of the calculated by ProLab z-scores with the tolerance limit $z=2$. Summary of the calculated z-scores are reported in table 4.

The Youden plots (figure 10-11) display a combined graphic of the results of two measurand-matrix combinations. Such a presentation allowed to identify systematic effects in the laboratory-specific deviations. It gave an immediate idea of the dominating sources of error in the results. Laboratories having results in the upper left or lower right hand corner of the diagram had analyses dominated by random error. Alternatively, laboratories having results close to the 45° line, but far away from the assigned value had results dominated by systematic error.

Data were processed a second time separately grouped by the two sample preparation methods (CR and AA). Methods were tested by statistical T-test and the results are shown in table 3. The experimental t values were smaller than both t critical values, which meant that results obtained by both methods did not differ significantly from each other.

Table 3. T-test for significance of the differences between the two sample preparation methods

	FORM01	FORM02	FORM03
Mean, Acetyl acetone (AA), mg/kg	6.68	15.59	26.35
Reproducibility s.d., mg/kg	0.45	1.00	1.54
number of labs	31	31	31
Mean, Chromotropic acid (CR), mg/kg	6.76	16.17	26.98
Reproducibility s.d., mg/kg	0.87	1.36	2.41
number of labs	31	31	31
s^2	0.4797	1.4248	4.0899
s	0.6926	1.1936	2.0223
t experimental	0.45	1.91	1.23
t crit (0.05, 60)	2.00	2.00	2.00
t crit (0.01, 60)	2.66	2.66	2.66

10. Comments on results and conclusions

24 laboratories returned their answers to the questionnaire on their experience with formaldehyde determination. A compilation of the answers showed that most of NRLs had already some experience with formaldehyde determination in food/food simulants. More than 90% of the laboratories used the CEN 13130-23 method.

The results of the ILC01 2011 showed that the participation of the laboratories in the ILC01 2011 was very satisfactory. 61 participants (98.4%) reported results out of 62 to whom sample kits had been sent. Six participants reported results obtained using two different sample preparation methods. 4 participants did not report 4 replicates for each concentration level.

Considering the z-scores, the overall participation was also quite satisfactory. Summary of the results as z-scores reported in table 1 and figures 6-9 showed good performance with more than 86.5% successful results by the laboratories for most of the measurand-matrix combinations. 52 laboratories (more than 85%) including all NRLs had all successful results.

Data were processed a second time separately grouped by the two sample preparation methods CR-chromotropic and AA-acetylacetone. In all three samples robust mean of the data from CR method resulted in higher value than the robust mean from AA method. Nevertheless, the statistical T-test showed that the results obtained using CR method did not differ significantly from the results obtained by the AA method. These two methods can thus be considered interchangeable.

Fig. 4

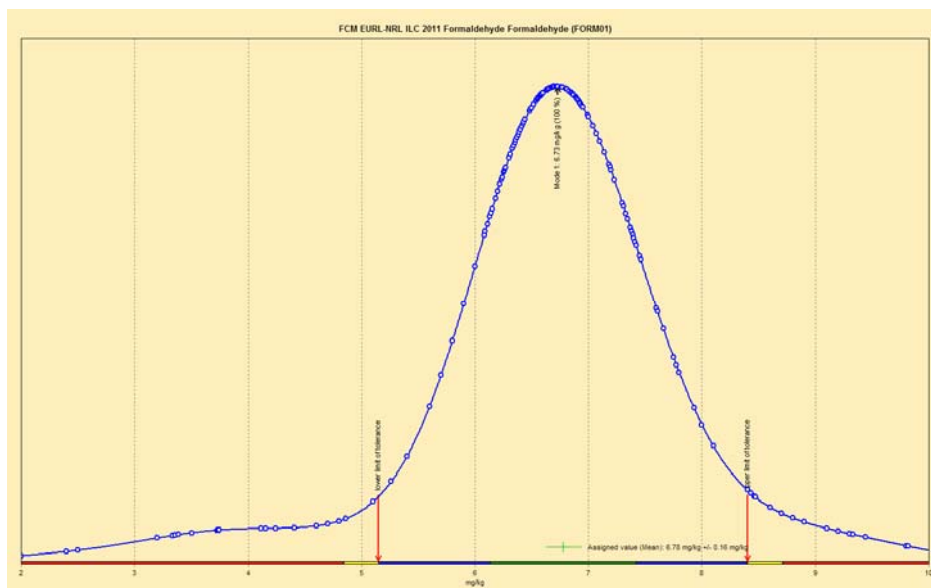


Fig. 5

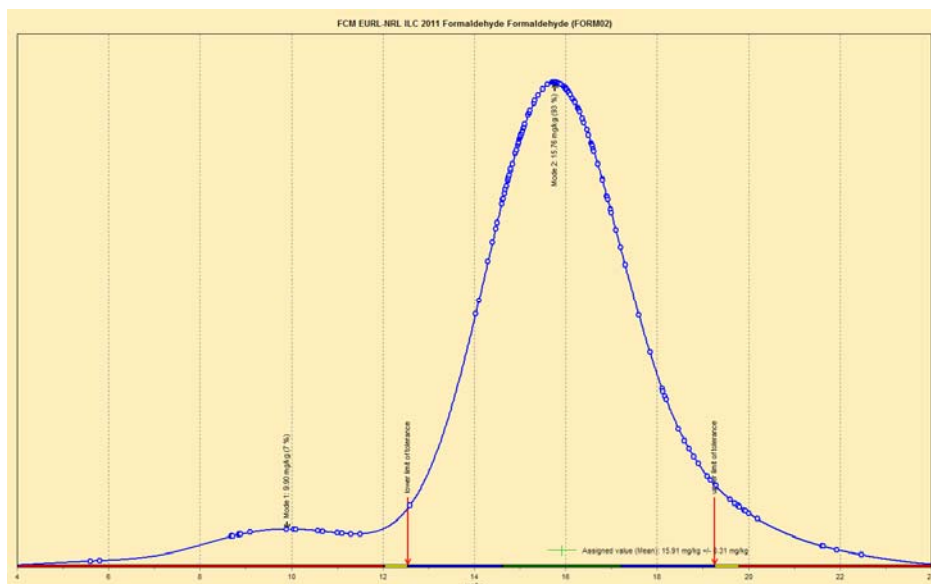


Fig. 6

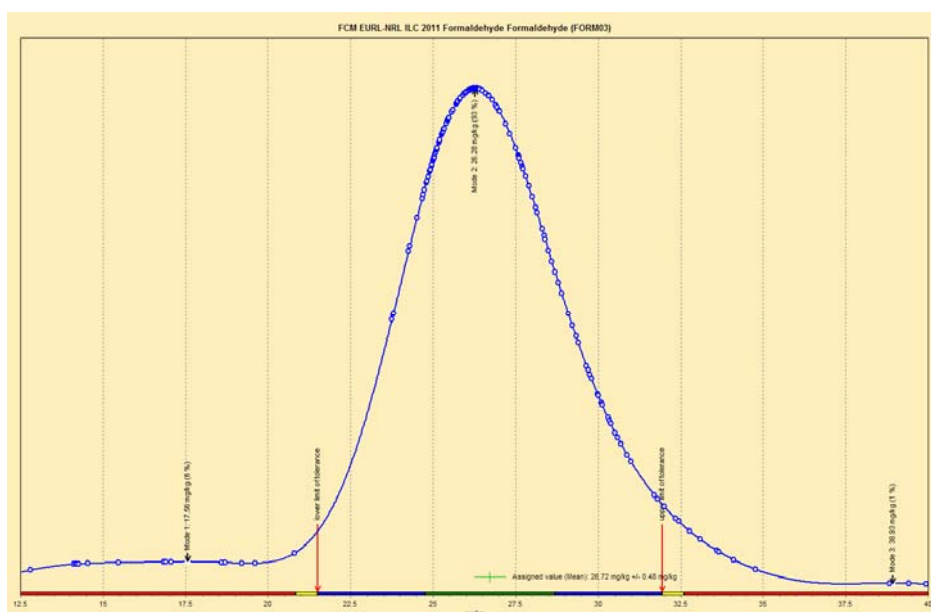


Figure 4-6. Kernel density plot of laboratory results (FORM01, FORM02, FORM03)

Table 4. Laboratories' corresponding z-scores

Laboratory	FORM01	FORM02	FORM03	Laboratory	FORM01	FORM02	FORM03
LC0001	0.10	0.38	0.07	LC0068	-0.39	-0.49	-0.60
LC0002	-0.19	-0.18	-0.23	LC0069	-0.25	-0.51	-0.20
LC0003	1.44	1.40	1.28	LC0070	-0.57	-0.69	-0.66
LC0004	0.52	0.24	-0.45	LC0071	-0.71	-0.21	-0.10
LC0005	-0.03	-0.69	-0.31	LC0072	-0.10	-0.12	0.01
LC0006	-0.16	-0.18	-0.23	LC0073	0.67	0.40	0.45
LC0007	-0.67	-0.83	-0.95	LC0074	-0.62	0.64	0.02
LC0010	0.09	-0.20	-0.70	LC0075	-2.56	-2.86	-3.10
LC0011	-0.19	-0.28	-0.32	LC0076	-2.11	-2.30	-4.49
LC0013	0.18	0.37	-0.15	LC0077	-0.06	-0.21	-0.17
LC0016	0.25	0.02	-0.12	LC0078	0.40	0.65	1.22
LC0017	-0.05	-0.17	-0.17	LC0079	-3.14	-3.34	-3.74
LC0018	-0.68	-0.50	-0.34	LC0080	-0.59	0.37	0.04
LC0020	-0.58	-0.76	-0.69	LC0081	-4.16	-4.16	-4.81
LC0021	0.52	0.41	0.74	LC0082	0.02	0.06	0.20
LC0025	-0.32	-0.53	-0.69	LC0083	0.12	-0.09	-0.20
LC0027	2.05	2.35	2.33	LC0084	-0.37	0.00	-0.15
LC0028	-0.18	-0.01	-0.29	LC0085	0.55	0.76	0.69
LC0029	-0.46	-0.66	0.18	LC0086	0.09	0.12	-0.06
LC0031	0.90	0.44	0.42	LC0087	1.12	1.48	1.41
LC0032	-0.10	-0.02	-0.11	LC0088	-5.23	-4.77	-2.74
LC0033	-0.50	-0.69	-0.19	LC0089	0.70	0.37	0.82
LC0034	2.61	2.20	2.64	LC0091	0.53	0.22	-0.32
LC0037	-0.06	-0.91	-0.39				
LC0038	0.25	0.00	-0.26				
LC0039	3.32	3.58	4.80				
LC0040	-0.41	-0.58	-0.66				
LC0041	-0.10	0.09	0.00				
LC0044	0.43	1.84	1.83				
LC0048	-0.43	-0.09	-0.03				
LC0049	0.12	-0.01	-0.69				
LC0050	0.05	0.12	-0.19				
LC0053	0.14	0.22	0.20				
LC0054	0.74	0.56	1.30				
LC0055	-0.37	-0.26	-0.37				
LC0056	0.24	-0.50	0.29				
LC0060	0.85	1.45	1.22				
LC0061	0.21	0.06	0.30				
LC0062	-3.74	-4.29	-5.34				
LC0063	-0.43	-0.52	-0.55				
LC0064	-0.78	-0.72	-0.64				
LC0065	-0.41	-0.42	-0.62				
LC0066	-1.57	-0.59	-0.42				
LC0067	2.30	1.63	1.34				

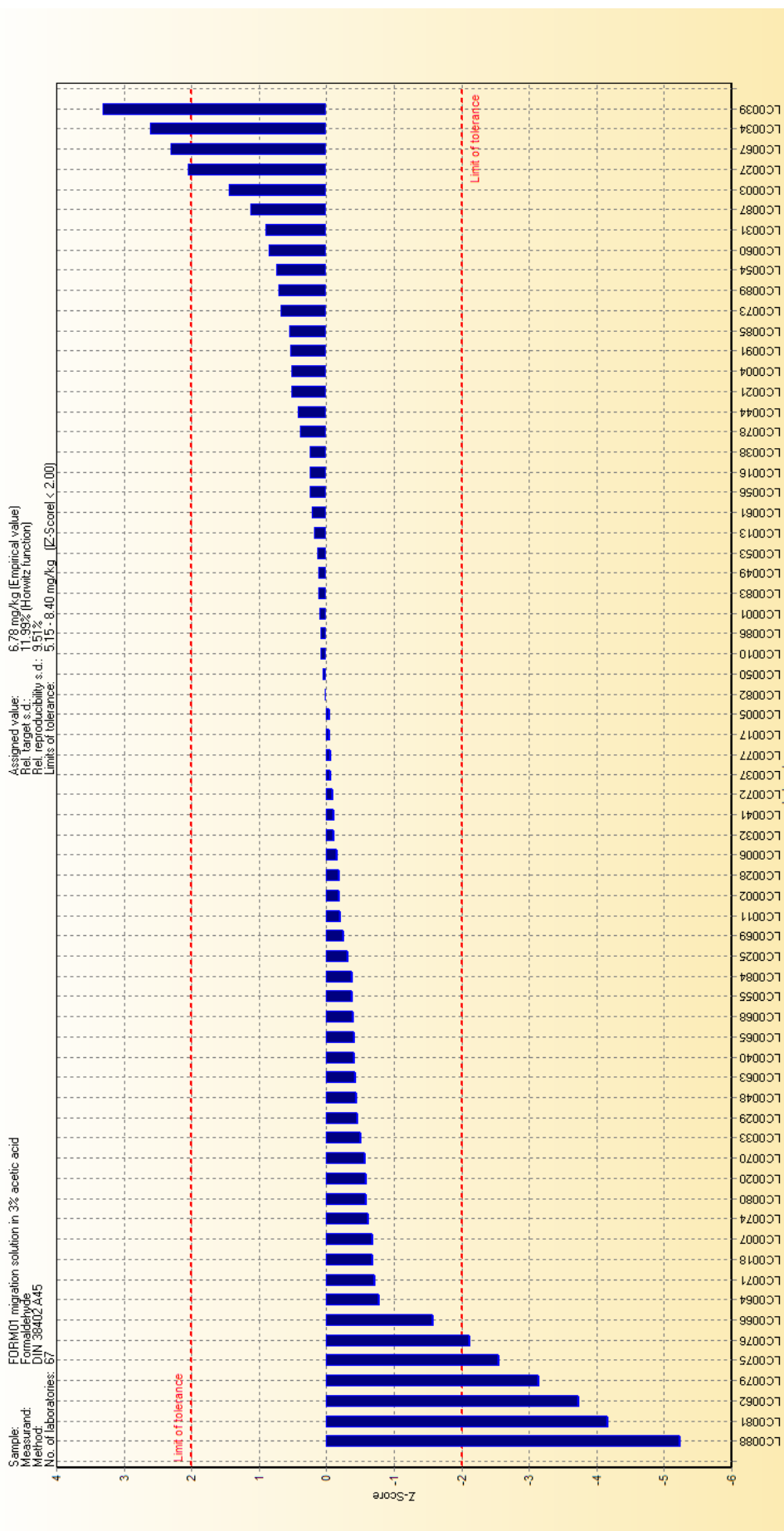


Figure 7. Summary graph of the laboratory's z-scores (FORM01)

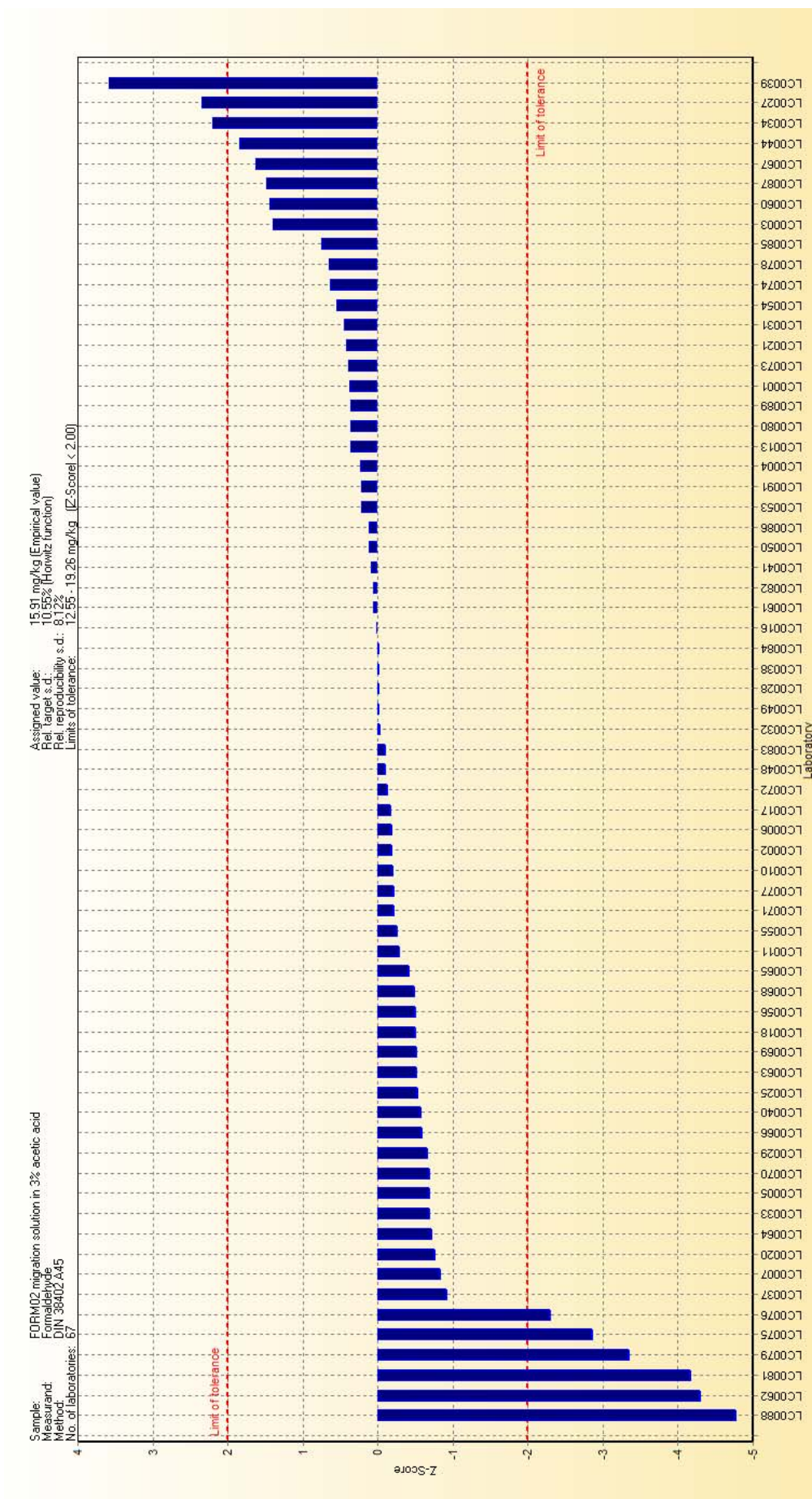


Figure 8. Summary graph of the laboratory's z-scores (FORM02)

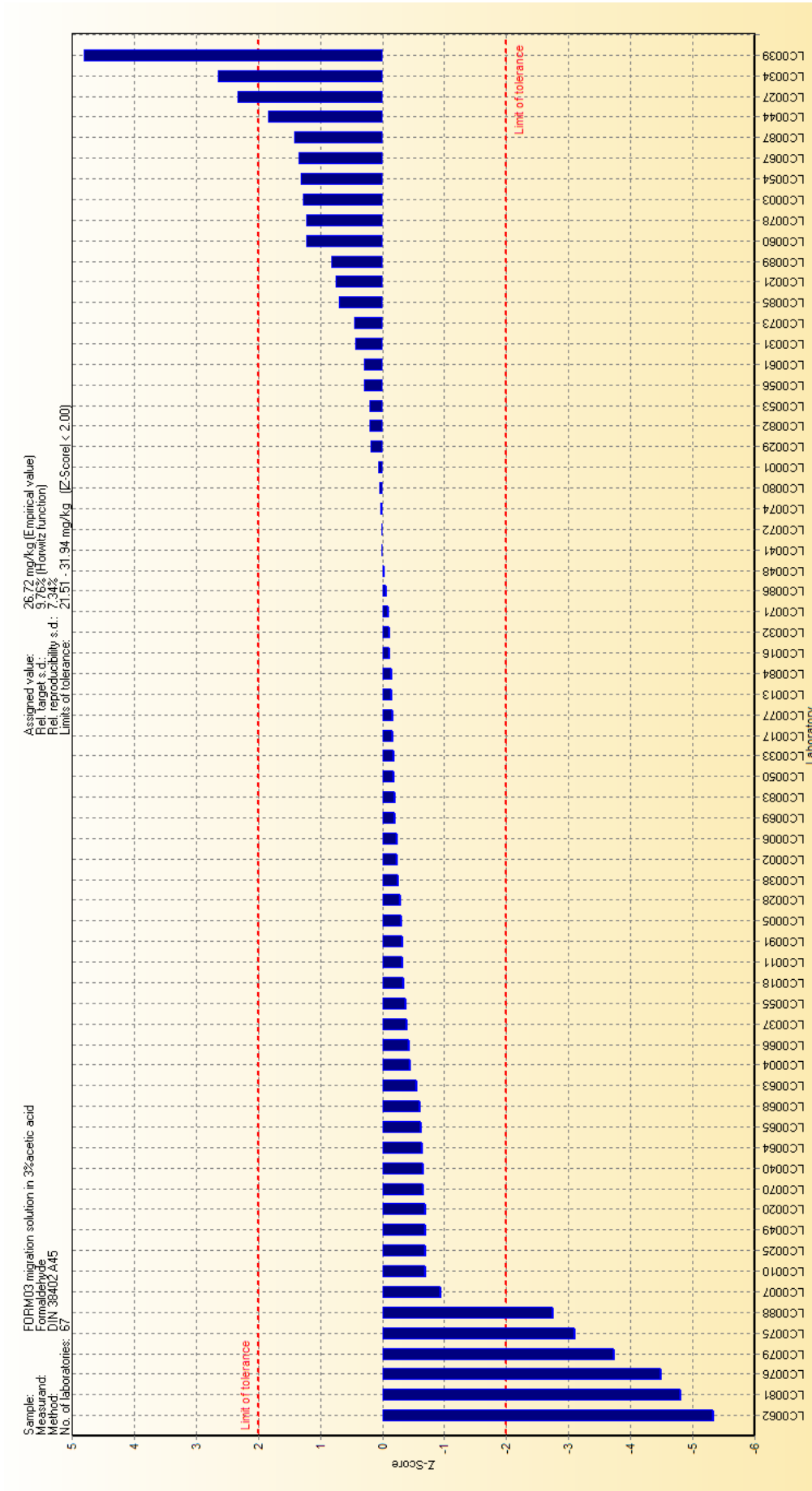


Figure 9. Summary graph of the laboratory's z-scores (FORM03)

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Fig.10

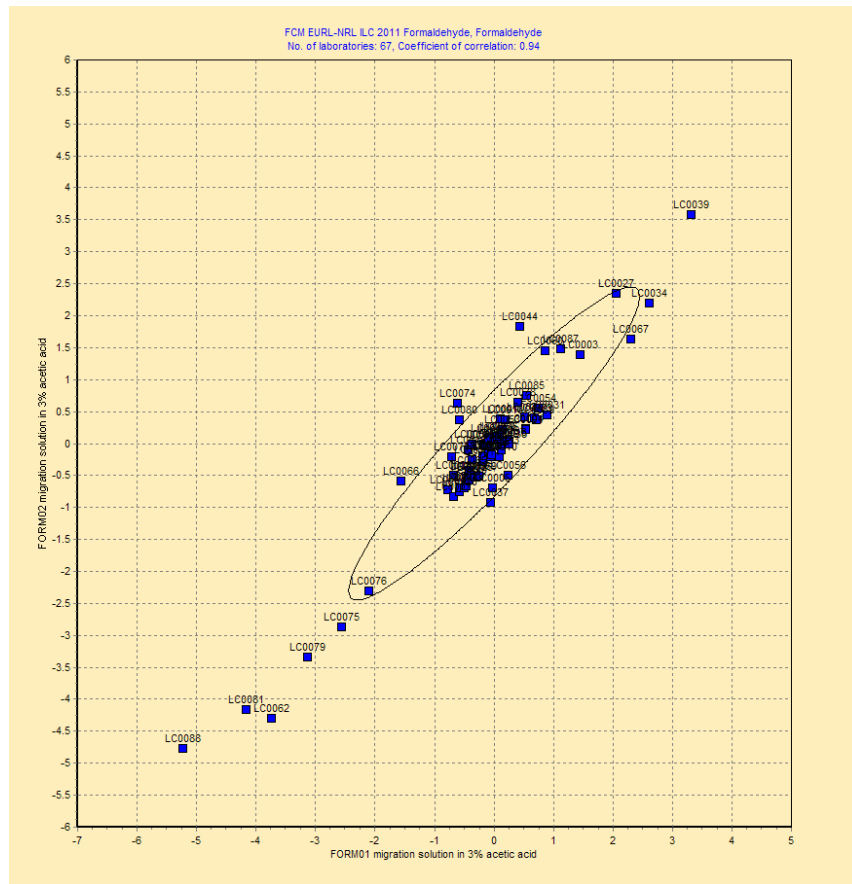


Fig.11

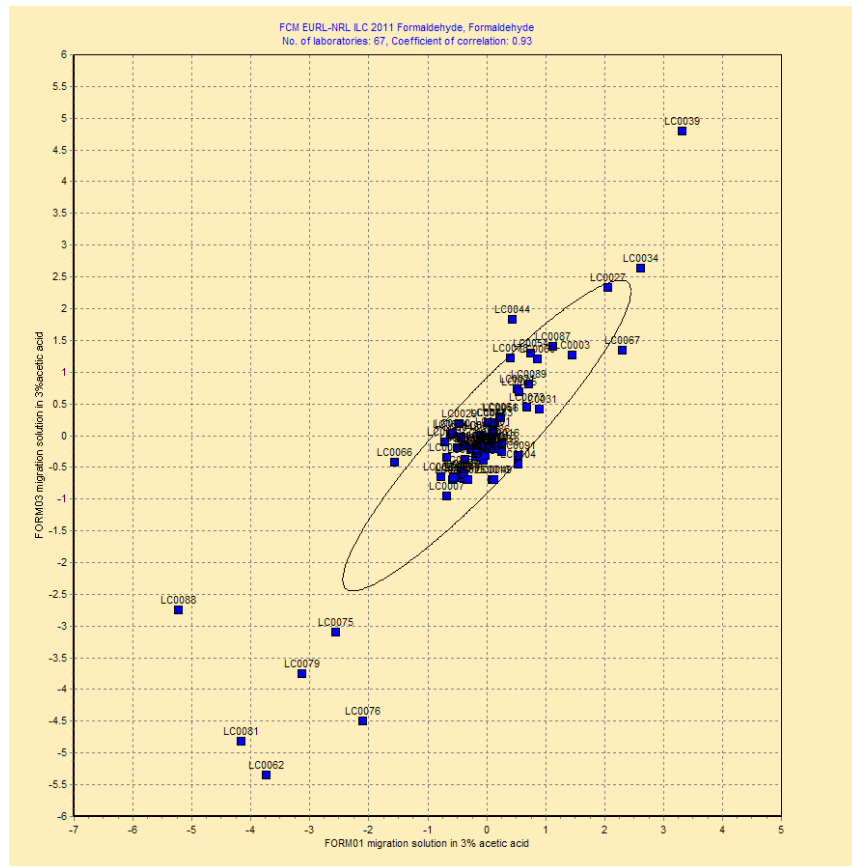


Figure 10-11. Youden plots of z-scores for formaldehyde between FORM01-FORM02 and FORM02 - FORM03

11. Acknowledgements

The NRLs and guests participating in this exercise - listed below - are kindly acknowledged.

NRLs

AUSTRIA	Austrian Agency for Health and Food Safety (AGES)
BELGIUM	Institute of Public Health, ISSP-LP
BULGARIA	National Centre for Public Health Protection, Sofia
BULGARIA	Regional Health Inspection, Veliko Tarnovo
REPUBLIC OF CYPRUS	Laboratory for Control of Food Contact Materials and Control of Toys Ministry of Health, State General Laboratory (SGL)
CZECH REPUBLIC	NIPH- NRL for Food Contact Materials and for Articles for children under 3 years old, National Institute of Public Health (SZU')
DENMARK	Department of Food Chemistry, National Food Institute Technical University of Denmark
ESTONIA	Health Protection Inspectorate - Central Laboratory of Chemistry
FINLAND	Finnish Customs Laboratory
FRANCE	Centre for Energy Material and Packaging - Laboratoire National d'Essais
FRANCE	SCL Laboratoire de Bordeaux-Pessac
GERMANY	Bundesinstitut für Risikobewertung (BfR) (Federal Institute for Risk Assessment)
GREECE	General Chemical State Laboratory, D' Chemical Service of Athens, Section Laboratory of Articles and Materials in Contact with Foodstuffs
HUNGARY	Central Agricultural Office, Food and Feed Safety Directorate
IRELAND	Public Analyst Laboratory - Sir Patrick Duns Hospital
ITALY	Istituto Superiore di Sanità, Laboratorio Esposizione e rischio da materiali, c/o Dipartimento ambiente e connessa prevenzione primaria
LUXEMBOURG	Laboratoire National de Santé, Division du Contrôle des Denrées Alimentaires
LATVIA	National Diagnostic Centre, Laboratory of Food and Environmental Investigations (LFEI)
LITHUANIA	National Public Health Investigation Centre, Laboratory of Chemistry
POLAND	Laboratory of Department of Food and Consumer Articles Research, National Institute of Hygiene
PORTUGAL	ESB-SE (Portuguese Catholic University - Biotechnology College – Packaging Department)
SLOVAK Republic	National Reference Centre and Laboratory for material and articles intended to come into contact with food, Regional Public Health Authority In Poprad (RUVZ)
SLOVENIA	National Institute of Public Health of Republic of Slovenia, Department of Sanitary Chemistry
SPAIN	Centro Nacional de Alimentación, Agencia Española de Seguridad Alimentaria y Nutrición (AESAN)
THE NETHERLANDS	Food and Consumer Product Safety Authority (VWA), Ministry of Economic Affairs, Agriculture and Innovation
UK	Central Science Laboratory

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SPAIN	Centro Analitico de Inspeccion y Control de Calidad de Comercio Exterior, Madrid
SWISS	Service de la Consommation et des Affaires Vétérinaires, Genève
FRANCE	SCL, Oullins
PORTUGAL	CNE Centro Nacional de Embalagem, Porto Salvo

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- [11] ISO GUIDE 35:2006; Reference materials–General and statistical principles for certification.

13. Annexes

- Annex 1: Overview of the preliminary questionnaire
- Annex 2: Invitation letter to laboratories ILC01 2011
- Annex 3: Format for confirmation of participation to ILC01 2011
- Annex 4: Letters accompanying the sample ILC01 2011
- Annex 5: Letter of confirmation of receipt of ILC01 2011
- Annex 6: Form for the compilation of the results in non-electronic format
- Annex 7: Results of the homogeneity study
- Annex 8: Results of the stability study

Annex 1. Overview of the preliminary questionnaire

Lp.	Lab Code	Method accredited/validated		QC	PT	Method reference	Type of instrument			Sample preparation	
		accredited	validated				UV-vis	LC/UV	HS-GC-FID	Type food/simulant	sample work up
1	LC0013	ACCREDITATED ISO 17025	Y	Y	N	EN 13130-23	Y			3% AcA; 50% ETOH	chromotropic acid
2	LC0029	N	Y	without ref material	N	EN 13130-23	Y			3% AcA; water	chromotropic acid
3	LC0031		in development	N	N		Y			3% AcA	chromotropic acid
4	LC0056	CEN/TS 13130-23:2005 accredited (simulants); EN 717-3:2003 – accredited (wood toys); inhouse method is accredited for air	Y	Y	N	EN 13130-23; EN 717-3:2003	Y			3% AcA; 50% ETOH	pentane-2,4-dione in the presence of ammonium acetate
5	LC0040	ACCREDITATED ISO 17025	Y	Y	N		Y			3% AcA	pentane-2,4-dione in the presence of ammonium acetate
6	LC0028			Y spike	N	CEN 13130-23 : 2005	Y			water;3% AcA;olive oil	chromotropic acid
7	LC0049	N	N	N	N	CEN/TS 13130-23	Y			3% AcA; 50% ETOH	chromotropic acid
8	LC0055		EN ISO/IEC 17025	Y	N		Y			water, 3% acetic acid	pentane-2,4-dione in the presence of ammonium acetate
9	LC0020	Yes (EN 1541:2001; EN ISO 4614:1999)		Y	N		Y			water, 3% acetic acid	pentane-2,4-dione in the presence of ammonium acetate
10	LC0006	Y	Y	Y	N	STN P CEN/TS 13130-23, EN ISO 14184-1	Y	intend to use	intend to use	water, 3% acetic acid, ethanol (10%,50%,95%)	pentane-2,4-dione in the presence of ammonium acetate 0.1%, 2,4-DNPH
11	LC0050	accreditation foreseen March 2011	Y	Y	N	EN 13130-23	Y			3% AcA	chromotropic acid
12	LC0005	N	N	N	N		Y				pentane-2,4-dione in the presence of ammonium acetate
13	LC0070	Y	Y	Y comp 2labs	N	PN-EN ISO 4614 & CEN /TS 13130-23	Y				pentane-2,4-dione in the presence of ammonium acetate
14	LC0018	Y	Y		N			Y		3% AcA	acetate ammonium solution added with acetyl acetone,
15	LC0025	Y	Y		Y-textiles		Y	Y-cosmetics		3% AcA	pentane-2,4-dione in the presence of ammonium acetate
16	LC0021	Y ; EN 1541	Y	Y	Yes for EN 1541		Y			Water, acetic acid 3%	pentane-2,4-dione in the presence of ammonium acetate
18	LC0001	N	N		N	DIN EN 717-3				3% AcA	pentane-2,4-dione in the presence of ammonium acetate
23	LC0004	N	N	N		CEN/TS 13130-23:2005	Y			3% AcA	chromotropic acid
24	LC0041	N	N		N			Y			Deriving with dimedone0.2%; boiling 30min

Annex 2. Invitation letter to laboratories ILC01 2011



EUROPEAN COMMISSION
GENERAL DIRECTORATE JRC
JOINT RESEARCH CENTRE
Institute for Health and Consumer Protection – IHCP
Unit Chemical Assessment and Testing



Ispra April 26th, 2011

Dear Madam, Sir

Comparative trial ILC 2011 - 01 from EURL FOOD CONTACT MATERIALS
“Determination of formaldehyde in 3% acetic acid migration solution”

On behalf of the EURL for food contact materials, I would like to invite you to participate in a comparative trial/interlaboratory comparison (ILC) exercise for the determination of formaldehyde in 3% acetic acid migration solution which is due to start by the end of May. As agreed in the December EURL-NRL FCM plenary, the primary scope of this ILC exercise is a Proficiency testing. However, in view of the support to Regulation 284/2011, we would like to suggest to limit the methods to the two procedures included in EN 13130-23 (i.e. standard for food contact). This will also allow us to derive new and full precision data for the method.

I would like to remind you that it is a duty for you as an NRL-FCM to participate in the ILCs organised by the EURL-FCM since the work programme is decided with your agreement. For this reason we encourage all of you to actively participate in this exercise. There is no charge for participation. Feel free to involve your local controls.

We have pre-registered everyone, which means we will send test kits to all of you. We however need to receive the **proformat of your participation** for our own administrative purposes. Kindly send back the proformat **by 13th May** to: Giorgia Beldi (giorgia.beldi@irc.ec.europa.eu). If you need more test kits to involve more laboratories at the national level please let us know immediately by e-mail so we can prepare the test samples accordingly.

The samples will be sent to you by the **end of May**. You will find additional information in the kit sent and on the form “shipment test F”. You will also receive more detailed instructions for the compilation of the results. The deadline for submission of results is **17th June 2011**.

If you have any question, please contact C. Simoneau (catherine.simoneau@irc.ec.europa.eu).

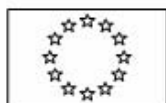
Sincerely yours,

Catherine Simoneau

Dr. Catherine Simoneau
Operating Manager, Community Reference Laboratory for Food Contact Materials
European Commission, DG-Joint Research Centre
Institute for Health and Consumer Protection
Unit Chemical Assessment and Testing, T.P. 260
Ispra Va 21020 Italy

Cc: MM. D. Kotzias (JRC), P. Castello (JRC), B. Larsen (JRC)
Mrs. A Schaefer, F. Vanhee (SANCO)

Annex 3. Format for confirmation of participation to ILC01 2011



EUROPEAN COMMISSION
GENERAL DIRECTORATE JRC
JOINT RESEARCH CENTRE
Institute for Health and Consumer Protection – IHCP
Unit Chemical Assessment and Testing



Ispra April 26th 2011
Annex to I2-MDV-EURL/CS/sm(2011)

**Participation to EURL-FCM ILC 2011 - 01
Interlaboratory comparison (ILC) exercise
for the determination of formaldehyde in 3% acetic acid migration solution**

CONFIRMATION OF PARTICIPATION

Your Name:	
Organization:	
Address:	
E-mail:	
Phone:	

item	YES	NO
I will participate the collaborative trial on analysis of formaldehyde in 3% acetic acid migration solution and will deliver results on time		
I have already the package with the files for filling the results and especially RingDat3.exe file from last year and I need only lab files for this year's ILC		
I don't have the package with the files for filling the results from last year		

Kindly send back this proformat to: Giorgia Beldi (giorgia.beldi@jrc.ec.europa.eu) by the **13th of May**.

The samples will be sent to you by the end of May. You will find additional information in the kit sent. The deadline for submission of results is **17th June 2011**.

Sincerely yours,

Catherine Simoneau

Annex 4. Letters accompanying the sample ILC01 2011



EUROPEAN COMMISSION
GENERAL DIRECTORATE JRC
JOINT RESEARCH CENTRE
Institute for Health and Consumer Protection – IHCP
Chemical Assessment and testing



Ispra 20th May, 2011

**Shipping kit for interlaboratory comparative testing EURL-FCM ILC01 2011 –
Formaldehyde in migration solutions of 3% acidic food simulant**

Shipping kit - samples

- FORM01, FORM02, FORM03– Three amber glass bottles with three real migration solutions from kitchen utensils in 3% acetic acid as food simulant.

Shipping kit - documentation

- letter of confirmation of receipt ILC 01 2011;
- letter with instructions for the compilation of the results for interlaboratory comparative testing EURL-FCM ILC01 2011
- a print copy of the excel form "ILC01 2011 test result form.xls" for information;
- electronic excel file "ILC01 2011 test result form.xls" will be sent by e-mail

Storage

- samples should be kept in the fridge at + 4°C.

Instructions

Result format: Use the personal "NAME.LAB" or the excel file "ILC01 2011 test result form.xls " that will be provided by e-mail;

Use the printed empty form "ILC01 2011 test result form.xls" in case of difficulties with the Pro-lab files.



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Institute for Health and Consumer Protection – IHCP
Chemical Assessment and Testing



Ispra May 20th, 2011

Instructions for the compilation of the results for interlaboratory comparative testing EURL-FCM ILC01 2011

DEADLINE: Friday, June 17th

Results requested:

Perform four replicates for each sample and report all the four replicate data using the unit of measure specified in the lab file or file "ILC01 2011 test result form.xls":

Compilation of results

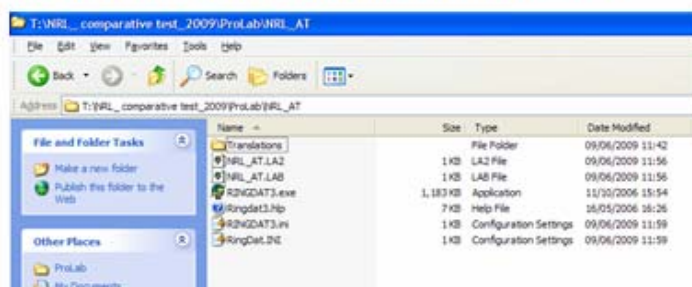
Data generated by the laboratories for the comparative test EURL-FCM ILC01/2011 will be processed by the EURL-FCM using a software package for statistical analyses and professional data handling of interlaboratory tests.

- a simple data entry program (RingDat3.exe) is provided to each participating laboratory (from previous ILC, available on the CIRCA website);
- two additional lab files with the extension "participant.LAB" and "participant.LA2", generated by the ProLab software are provided to each laboratory individually (personal files) by e-mail;
- the name of each laboratory and the samples are codified by the software, so that each participant will receive a sample with unique codified numbers (i.e., 0586);
- The "*.LA2" file contains information about the participant – laboratory name and laboratory code;
- The "*.LAB" file is unique to each laboratory (personal) and contains information about the samples (samples code) and measurands that have to be analyzed and reported.

Each laboratory has to start the RingDat3.exe program and to open "NAME.LAB" file for reporting the results. A table will appear with cells for every measurand/sample combination. That is why 3 sample codes will appear for each participantfile – one for each concentration level.

Procedure to be followed by laboratories for the opening the LAB files from the software.

First: Create a folder on your computer and transfer RingDat files and Translation directory (from last year ILC or from CD-ROM 2010) into it. Copy there as well the "NRL_X.LAB" and "NRL_X".LA2 files which you'll receive by mail. The folder should contain:



Direct access EURL: ph: +39.0332.785889 Fax: +39.0332.785707 e-mail: catherine.simonea@jec.europa.eu <http://orl-fcm.jrc.it/>

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Chemical Assessment and Testing

Then:

- Open the file "RINGDAT3.exe"
- Click on "Open" command
- Select the "NRL_X.LAB" file (where X is the member state abbreviation- with one to three letters) and click on "Open" command using the button on the top menu of the window
- Windows you should see using the software is :

Sample code	Measurand	Description	Unit	Value 1	Value 2	Value 3	Value 4
ACN10471	DIDP	DIDP	mg/kg				
ACN20463	DIDP	DIDP	mg/kg				
ACN30542	DIDP	DIDP	mg/kg				
OIL10376	DIDP	DIDP	mg/kg				
OIL20236	DIDP	DIDP	mg/kg				
OIL30338	DIDP	DIDP	mg/kg				

- Fill the table with your data
- Save the file using the button on the top menu of the window
- Send only the "NRL_X.LAB" file by e-mail to Giorgia Beldi (giorgia.beldi@irc.ec.europa.eu)

Please fill your results and send it back by e-mail to Giorgia Beldi (giorgia.beldi@irc.ec.europa.eu) by June 17th.

If you have any question, please contact Catherine Simoneau (catherine.simoneau@irc.ec.europa.eu), ph. +39.0332.785889

Sincerely yours,

Catherine Simoneau
Dr. Catherine Simoneau
Operating Manager, EU Reference Laboratory for Food Contact Materials
European Commission, DG-Joint Research Centre
Institute for Health and Consumer Protection
Unit Chemical Assessment and Testing, T.P. 260
Ispra Va 21020 Italy

Annex 5. Letter of confirmation of receipt of ILC01 2011



EUROPEAN COMMISSION
GENERAL DIRECTORATE JRC
JOINT RESEARCH CENTRE
Institute for Health and Consumer Protection – IHCP
Chemical exposure and testing



Ispra May 20th , 2011

**PARTICIPATION TO CRL-FCM ILC01 2011
FORMALDEHYDE IN 3% ACETIC ACID**

CONFIRMATION OF RECEIPT OF THE SAMPLES

Please return this form to confirm that the sample package has arrived. In case the package is damaged, please state this on the form and contact us immediately.

Your Name:	
Organization:	
E-mail:	
Phone:	

Any remarks

Date arrival package

Signature

Kindly send back this form to: Giorgia Beldi (giorgia.beldi@jrc.ec.europa.eu)

Sincerely yours,

Catherine Simoneau

Dr. Catherine Simoneau
Operating Manager, EU Laboratory for Food Contact Materials
European Commission, DG-Joint Research Centre
Institute for Health and Consumer Protection
Unit CAT, T.P. 260
Ispra Va 21020 Italy

Annex 6. Form for the compilation of the results in non-electronic format

FCM EURL-NRL ILC01 2011 Formaldehyde

TEST RESULTS

Lab Code - LC00....

Sample code	Measurand	Description	Unit	Date of analysis	Test result 1	Test result 2	Test result 3	Test result 4	Sample preparation*	Instrumental method**
	FORM01	Formaldehyde	mg/kg							repeat the instrumental method
	FORM02	Formaldehyde	mg/kg							
	FORM03	Formaldehyde	mg/kg							

* Chromotropic acid; Acetylacetone or other

** HPLC/UV; LC/MS; UV/VIS or other

.....
Place and date

.....
Laboratory Manager

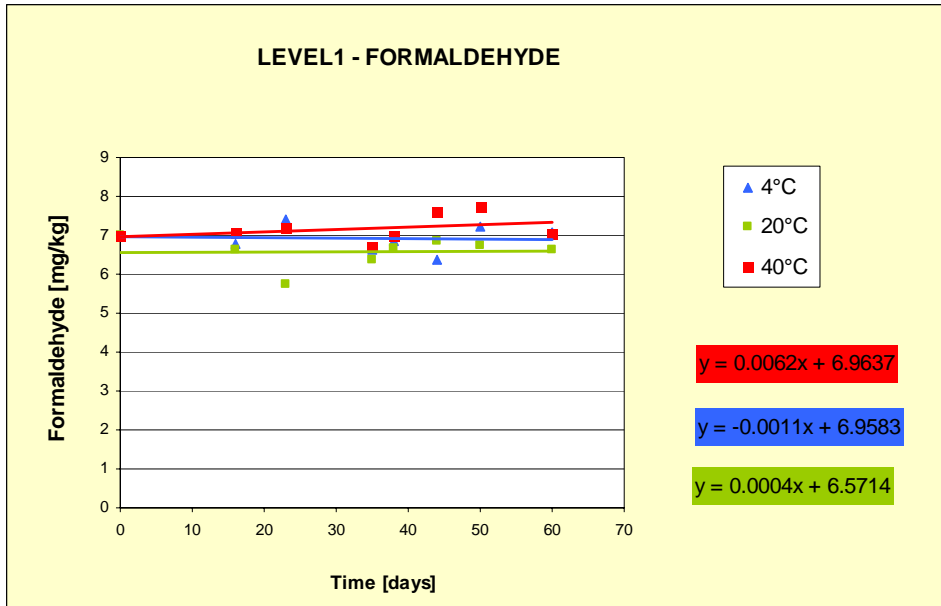
.....
Signature

Annex 7. Results of the homogeneity study

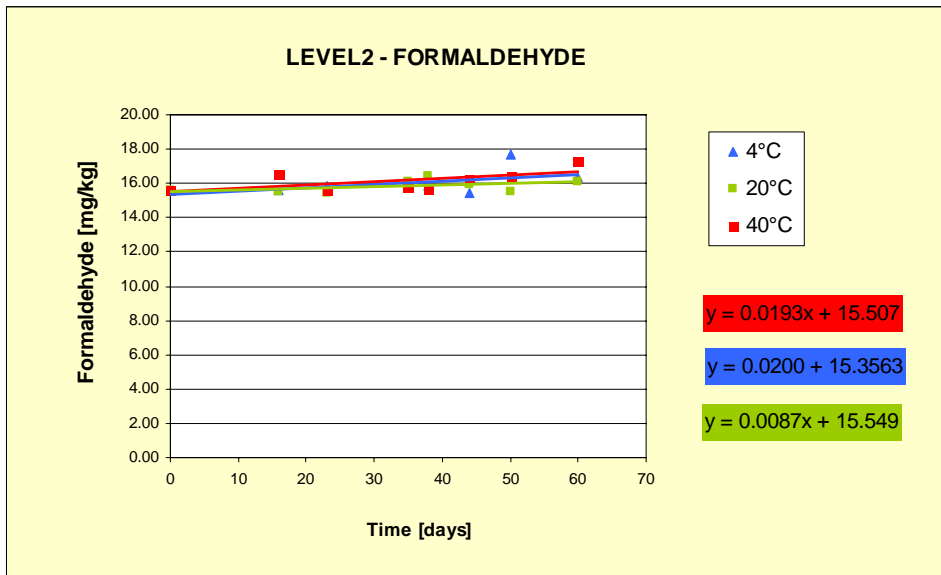
Sample	Measurand	Unit	Mean	s(analytical) %	s(samples) %	Mode s(target)	HORRAT	s(target) %	F-test Check for significant heterogeneity	ISO 13528 Check for sufficient homogeneity	Harmonized Protocol - test on significant heterogeneity
FORM01	FORM	mg/kg	7.01	1.22	1.04	Horwitz	1	11.93	OK	OK	OK
FORM02	FORM	mg/kg	15.61	1.25	0.60	Horwitz	1	10.58	OK	OK	OK
FORM03	FORM	mg/kg	25.21	1.45	1.35	Horwitz	1	9.84	OK	OK	OK

Annex 8. Results of the stability study

A)



B)



C)

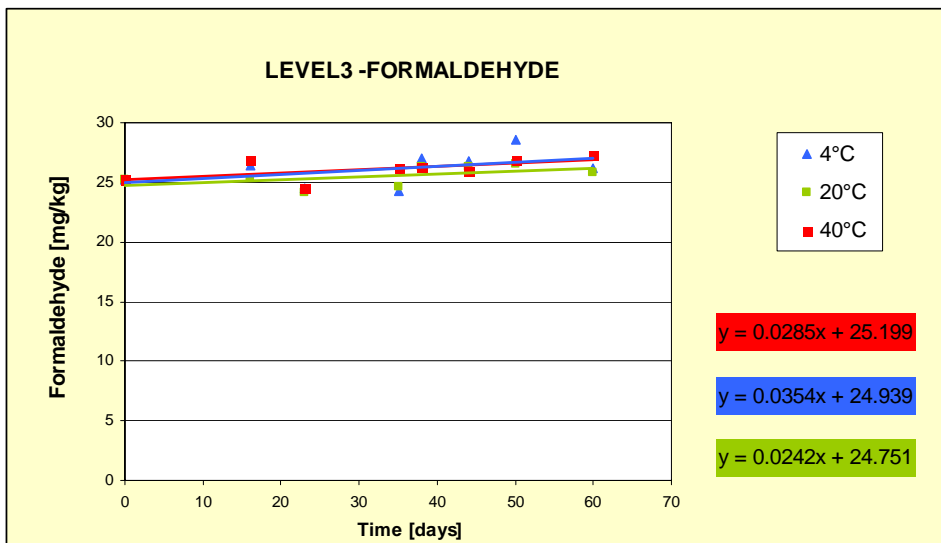


Figure 12. Results of the stability studies for A) FORM01, B) FORM02 and C) FORM03

European Commission

EUR 25226 EN – Joint Research Centre – Institute for Health and Consumer Protection

Title: Report of the interlaboratory comparison Formaldehyde in food contact migration solution,

Author(s): G. Beldi, N. Jakubowska, M. Derda and C. Simoneau

Luxembourg: Publications Office of the European Union

2012 – 38 pp. – 21 x 29 cm

EUR – Scientific and Technical Research series – ISSN 1831-9424

ISBN 978-92-79-23111-7

doi:10.2788/13916

Abstract

This report presents the results of the Inter-laboratory comparison (ILC) organised by the EURL-FCM, Ispra (Italy), which focus on the quantification of formaldehyde in migration solutions of 3% acetic acid from food contact materials. The test materials used for preparation of the migration solutions were melamine kitchenware (spoons) containing formaldehyde. The EURL prepared and distributed three concentration levels of migration solution. The general aim of the exercise was to assess the proficiency of the official control laboratories and consequently the participants were free to use any analytical method of their choice, however CEN 13130-23 method was suggested. There were 62 participants to whom samples were dispatched (27 national reference laboratories (NRLs) + 35 national control laboratories) and 61 of which submitted results. The homogeneity and stability studies were performed by the EURL-FCM laboratory. The assigned values were obtained after applying the robust statistics to the results of the participants. Participants were invited to report four results for each concentration level. This was done by most of the participants. Laboratory results were rated with z-scores in accordance with ISO 13528 [1], standard deviations for proficiency assessment (also called target standard deviations) were set based on Horwitz equation. As a conclusion of the ILC exercise on the quantification of formaldehyde in the migration solution of kitchenware in 3% acetic acid, this ILC showed that the participation in the ILC was satisfactory regarding the number of the participating laboratories. From the EURL-NRL network all 27 laboratories reported results. One participant did not send any results. 52 laboratories (more than 85%) including all NRLs had all results successful and for 8 participants all results were unsatisfactory. Data were processed a second time separately grouped by the two sample preparation methods CR-chromotropic acid and AA-acetyl acetone. Statistical T-test shows that the results obtained using CR method do not differ significantly from the results obtained by second - AA method. These two methods are interchangeable.

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EURL – Food Contact Material. Formaldehyde in kitchenware

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