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VALIDATION OF CEN/TC 292 LEACHING TESTS AND ELUATE ANALYSIS METHODS PrEN 12457 1-4, ENV 13370 AND ENV 12506 IN CO-OPERATION WITH CEN/TC 308

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Part 10. Steering committee and participants

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VALIDATION OF CEN/TC 292 LEACHING TESTS AND ELUATE ANALYSIS METHODS PrEN 12457 1-4, ENV 13370 AND ENV 12506 IN CO-OPERATION WITH CEN/TC308

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1. INTRODUCTION

Before standard test methods can be used in a regulatory context, standards need to be validated to be able to know what quality in terms of repeatability and reproducibility can be expected. In relation to leaching, which is the topic of this validation study, one must realize that a leaching tests alone is not sufficient to come to a conclusion on environmental properties of a material. Sampling of waste and analysis of eluates are aspects that are an integral part of a judgement of leaching test results. In this work, the CEN/TC 292 compliance leaching test, EN12457 parts 1 - 4 and the Eluate analysis methods prEN 13370 and ENV 12506 have been validated. These standards are important in view of their use in the EU landfill Directive 1999/31/EC and possibly other related regulations to be developed in the future. The compliance leaching test cannot be used alone to determine the leaching behaviour of a waste. For basic characterisation a methodology for the determination of the leaching behaviour of waste has been developed within CEN/TC 292, which is formulated in ENV 12920: 1998 "Methodology for the determination of the leaching behaviour of waste under specified conditions". Validation of standards for waste can only be validated for a selection of representative wastes from the large number of wastes and waste types relevant in Europe.

2. SAMPLE COLLECTION AND PREPARATION

As no waste materials are available as a standard reference material in sufficient quantities for validation, the study was carried out on real wastes coming from industrial processes and prepared to be representative of real laboratory samples arising from primary sampling procedures. In this manner the results can be used directly to assess performance characteristics of the leaching test described in EN 12457 Parts 1 - 4.

As justification for the selection of materials, the materials cover a wide range of final pH values, which is one of the key parameters in leaching. In addition, the materials selected all occur in bulk quantities in Europe. MSWI Bottom ash (MBA - EWC 19 01 11) - Municipal Solid Waste Incinerator Bottom ash is an inherently heterogeneous material with a grain size distribution extending from very fine to relatively coarse. The concentration levels encountered in bottom ash are intermediate. Metalurgical slag (MES - EWC 10 04 01) - metallurgical slag is selected for its potentially high metal leachability. It comes in different particle size ranges to make it suitable for a comparison of particle size classes. The main feature to be tested on this materials is therefore the performance characteristics of Part 2 and 4 of EN 12457. A specific feature of the metallurgical slag is the relative low buffer capacity. This makes the material appropriate for the evaluation of the pH-conditions of the leaching test. Sand blasting material (SBW- EWC 12 01 16) - This material is relatively low in leachable elements. Sand blasting material is also relatively inert. In view of analytical capabilities a material with low, but measurable leachability is necessary. Sludge from chemical waste water plant (CHS - EWC 06 05 02) - This industrial sludge is an example of a waste with high moisture content. It can only be tested by EN 12457 Part 2. Filter cake of treated fly ash from waste incineration (FCM - EWC 19 01 05) - This material has a high soluble salt loading, which has consequences for the analysis of eluates with a low concentrations of elements. Sludge from municipal wastewater treatment (SEW - EWC 19 08 05) - This material is particularly relevant to CEN/TC 308. This is typically a material with a high water content. Therefore, only EN 12457 Part 2 is useful. In the municipal sludge the presence of high concentrations of dissolved organic matter provide a complex matrix for the analysis of the eluates. Contaminated soil (COS - EWC 17 05 03) - Contaminated soil is often designated as waste and very abundant all around Europe. Contaminated soil is usually a relatively fine-grained material. In this case, the main focus is on the low L/S conditions in EN 12457 Parts 1 and 3.

The materials have been processed by different laboratories to obtain laboratory samples for homogeneity testing, ruggedness testing, characterisation and for the ultimate validation by participating European laboratories. Based on the analytical data foundry sand (FS), which was included initially, has been rejected, as the concentrations in eluates were too low, the material is only relevant for phenol. The analysis of phenol is covered through eluate analysis. Homogeneity testing has indicated for which parameters validation would be possible with the wastes sampled.

3. RUGGEDNESS TESTING

A ruggedness testing programme has been carried out to assess the sensitivity of the leaching procedures prEN 12457 part 1- 4 to variations in several test conditions. The test was performed by varying one of 7 potentially critical test conditions at a time and compare the result of 5 replicates to the results of 10 replicates carried out under "standard" conditions for each parameter. All 4 parts were tested but the most thorough testing was carried out on EN 12457-2 alone since most of the test conditions and procedures are common for all 4 parts. The test conditions addressed were: contact time, liquid to solid ratio (L/S), weight of test material, temperature, mode of agitation, diameter of the filter and size reduction of test material. A few additional test conditions, including head space and particle size, were addressed using a factorial design experiment. Four materials were tested: MSWI bottom ash (MBA), filter cake of treated MSWI fly ash (FCM), contaminated soil (COS) and sewage sludge from a municipal wastewater treatment plant (SEW). All parts of the test were performed on MBA whereas only part 2 (L/S = 10 l/kg) were performed on the other materials. The choice of analytical parameters to be addressed in the test were based mainly on the nature of the materials, the levels of concentration in the eluates and the analytical capabilities of the participants. They were: MBA (Ba, Cr, Cu, Mo, Pb, Sb, Zn, Cl^-, S/SO_4^{2-}), FCM (Ba, Cd, Cr, Mo, F^-, Cl^-, NO_2^-, Cr(VI)), COS (As, Cd, Co, Ni, Pb, Sb, Zn) and SEW (B, Ba, Cd, co, Cu, Mo, Ni, Pb, Sn, Zn, NH_4^+, SO_4^{2-}, DOC). Effects were generally evaluated at a 1% level of significance.

Contact time was tested for variations of ± 2 hours, whereas only variations of ± 0.5 hours are allowed by the draft standard. The results indicate that contact time variations within the ranges prescribed by the draft standard do not appear to have any significant influence on the test result. The results of the factorial design experiment indicate that the settling time prior to filtration (0 – 15 minutes) is not critical.

The variations of the L/S ratio in the test were ± 10 % of the designated value, whereas the variations allowed by the draft standard are only 2 %. The larger variation turned out to be critical for a number of parameters, but a subsequent further analysis of the data indicated that variations within the L/S ranges allowed by the standard are unlikely to influence the results significantly. It should be noted that solubility controlled components are most sensitive to changes in L/S when the results are reported in terms of leached amount (mg/kg), whereas availability controlled components are most sensitive when results are reported in terms of eluate concentration (mg/l).

The sensitivity to the weight of the test material was tested at 50 g and 200 g with the prescribed standard value of 100 g (with the prescribed L/S value). This is a much wider range than the ± 5 g allowed by the draft standard. The general ruggedness test indicated that the wide range of variation did have a significant effect on the results for a few components. The factorial test design experiment showed that for some of these components ( ) the effect observed could be ascribed to variations in headspace. This has led to recommendation and implementation of changes to the draft standard aimed at ensuring a constant and limited headspace in the leaching

vessels. The results indicate that the use of small portions of material may affect the results due to heterogeneity effects for some parameters( ). It is therefore likely that the use of test portions smaller than those prescribed in the standard is more critical than the use of larger portions.

In the ruggedness testing the temperature was varied between 10 °C and 30 °C, whereas the range allowed by the draft standard is 15 °C – 25 °C. The tested variation did have a significant effect on the test results for several components( ). Further analysis of the data indicated that a range of variation corresponding to that prescribed by the standard would have a significant effect only for Ba. The maximum effect of this temperature variation on the amount of Ba leached was estimated to be within the order of ± 20 %. Since temperature does have an effect, a change in the temperature specifications of the standard from 15 °C – 25 °C to 20 °C ± 5 °C has been recommended and implemented. This change signals more clearly that 20 °C is the target temperature.

The effect of the mode of agitation was tested using an end over end tumbler, a roller table and a wrist shaker, respectively. The results indicated that the mode of agitation does have a significant effect on the results for several components. Based on the results it was recommended and implemented into the draft standard that only end-over-end tumbling and roller tables should used for agitation. It its further recommended that any roller table used should have eccentric motion and that only round (as opposed to square) bottles are to be used.

Filter sizes between 47 and 147 mm were tested. The filter size is not specified in the draft standard, but it was shown to have a significant effect on the results for several components( ). Due to lacking information on filtration flow rates, the results could not be evaluated in-depth. The results do, however, stress the importance of the filtration procedure and of observing the prescribed minimum flow rate (and of reporting the actual flow rate). The results of the factorial design experiment indicated that it is unimportant whether the filters are made of cellulose esters or vinyl fluoride. The results also indicated that the use of pressure filtration instead of vacuum filtration only had a significant influence of the result for Pb.

The mode of size reduction applied to the test material (jaw crusher, hammer mill and rotary disc mill) does have a significant influence on the results for several components( ). It has therefore been recommended and implemented into the draft standard that only a jaw crusher should be used for size reduction of the material.

The practical work with the draft standards prEN 12457 part 1-4 during the ruggedness testing have given rise to some additional observations and recommendations for changes: In the draft standard a filtration vacuum of 2500 Pa to 4000 Pa (25 to 40 mbars) is prescribed. This is far too little to have any influence on the filtration, and it is recommended to change the range to 30000 – 70000 Pa (300 to 700 mbars). A normal water ejection pump typically operates in the vicinity of 50000 Pa.

In the standard pre-rinsed filters are prescribed. This is probably a remnant from previous times when it was necessary to rinse the filters. Today very clean filters are available and the prescribed rinsing procedure is unnecessary and it actually makes the filters less stable. It is therefore recommended to change the wording to „Pre-rinsed or similarly clean 0.45 µm filters…"

The standards modified according to the results from the ruggedness testing have been circulated for the final validation work.

4. CHARACTERIZATION OF LEACHING BEHAVIOUR

In CEN/TC 292 Working group 6 leaching behaviour tests have been developed (PrEN 14405 and PrEN 14429), which play an important role in understanding leaching behaviour of wastes and provides a basis for long-term behaviour. Long term behaviour forms the basis for regulatory limit setting. The characterisation data presented provide a basis of reference that allow conclusions to be drawn on behaviour of materials under different exposure conditions than those tested in a leaching test. In particular, the pH dependence test data provide information on the chemical speciation of elements in the various matrices. The information also allows to identify particular sensitivity to pH differences in testing. Factors that control leachability in specific matrices can be recognised (e.g. role of DOC, control of leachability by common mineral phases).

The agreement between EN 12457 results and respectively the pH dependence leaching test and the percolation leaching test (at the corresponding pH and L/S=10 condition) is generally good (figure 1).

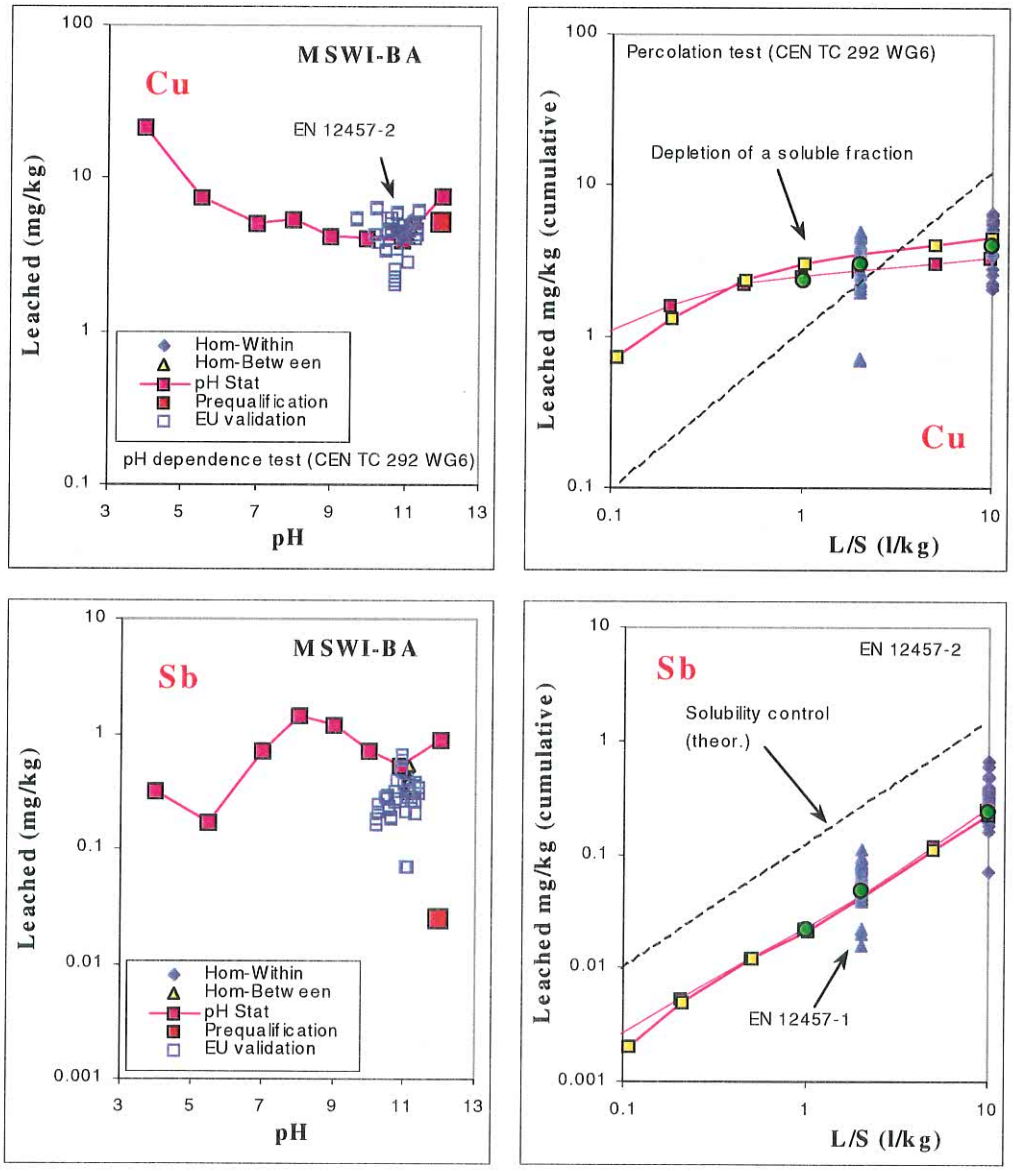


Figure 1 *Relationships between CEN TC 292 characterisation and compliance leaching tests. MSWI BA is Municipal Solid Waste Incinerator Bottom ash.*

In this figure also data from the pre-qualification to determine the sample suitability, the homogeneity testing are included. Those data fall well within the cluster of data points resulting from the EU wide validation study. The elements Cu and Sb are shown here to illustrate the difference in leaching behaviour : Cu washout of soluble species - Sb solubility control. For other elements, differences can occur in case of measurements close to the detection limit or in cases where relatively large changes in pH or other controlling parameters occur over the course of the percolation test. The relationship between compliance tests and characterisation tests is important, as characterisation tests provide the basis for long term leaching behaviour of materials, for which the compliance tests form a quick check for quality and consistency.

5. SUB-SAMPLING

In judging performance of (sub-) sampling methods, the analytical sensitivity plays an important role. Preferably this factor should be ruled out by selecting parameters with sufficient analytical sensitivity in judging sub-sampling performance.

Sub-sampling performance may be very element specific, as a material may be homogeneous for many, but not for all constituents of interest. This requires more knowledge of the material under consideration. Cone and quartering and sampling with a riffler are suitable methods for sub-sampling in the laboratory.

The results indicate that sub-sampling from 4 mm size reduced laboratory samples show the lowest relative standard deviations and may be judged therefore as is the more appropriate method. At 0-10 mm the relative standard deviation is slightly higher than for 0-4 mm. Significantly larger relative standard deviations in sub-sampling are noted for the 0-40 mm fraction.

In case of obvious sample heterogeneity, such as in MSWI bottom ash, analysis for composition may be less repeatable than analysis by leaching in spite of the higher concentration levels, which are to be measured by total chemical analysis (Table I). In case of Cu this heterogeneity can be understood from the presence of non-leachable pure metal particles such as originating from staples and electrical wire clippings.

Table I *Comparison of results of sub-sampling on leaching versus composition analysis All data in mg/kg.*

			Grab			Cone&Quarter			Riffler		
			Avg*	Std	Rstd %	Avg	Std	Rstd %	Avg	Std	Rstd %
Composition		Cu	5510	3695	67	2153	691	32	3290	2513	76
Leaching	40 mm	Cu	0.51	0.03	6.7	0.48	0.09	18	0.53	0.05	9.8
	10 mm	Cu	0.58	0.05	8.8	0.59	0.06	11	0.57	0.05	8.9
	4 mm	Cu	0.51	0.05	10	0.55	0.03	5.6	0.50	0.04	7.6
Composition		Ba	813	346	43	684	59	8.7	642	83	12.9
Leaching	40 mm	Ba	0.128	0.003	2.55	0.123	0.007	5.55	0.119	0.004	3.03
	10 mm	Ba	0.113	0.002	1.75	0.110	0.002	2.22	0.107	0.004	3.51
	4 mm	Ba	0.107	0.004	3.50	0.106	0.002	1.90	0.102	0.003	3.10

*Avg = Average; Std = standard deviation; Rstd = relative standard deviation.

Heterogeneity may appear in forms that are unrelated to environmental impact, such as in case of metals (e.g Pb, Cu, Zn) in MSWI bottom ash. The metals although presnet in relatively high

content do not significantly contribute to leaching. In such cases, leaching is the preferred method of assessing environmental properties of materials.

Sub-sampling in the laboratory for testing should be carried out after size reduction to within the specified particle size range for the standard (respectively 4 and 10 mm). Under this condition the additional variability caused by sub-sampling is minimised. Separation of a test portion meeting the requirements by the standard by sieving is not allowed.

Apart from the 0-40 mm material, the relative standard deviation within a size/sub-sampling method combination does not vary very much between the size/sub-sampling method combinations. The differences are mainly between the elements analysed, which is largely related to the concentration levels measured.
For MBA the variability within sampling method/ size combinations (n=5) for the elements analysed in the EU wide validation of EN 12457-2 corresponds well with the within laboratory variability on the test method as determined in the validation of EN 12457 -2 (See part 5). This implies that the contribution of sub-sampling to the overall uncertainty in performing a leaching test is limited.
In previous work carried out in the preparation of EN 12457, the result obtained for batch tests carried out on the same material with different particle size distributions meeting the requirements of the respective standards is significantly larger than the reproducibility limit obtained for such a standard. This implies that particularly with EN 12457-4, in which a statement is given on its application to even larger particle sizes (up to 40 mm), the user must be well aware of the effects of particle size on the test result.

6. STANDARD ELUATE

For a proper evaluation of analytical performance of participating laboratories a Standard Eluate has been prepared to be analysed by all participants in the ruggedness testing, in the validation of EN 12457 and in the validation of eluate analysis methods EN 13370 and EN 12506. The Standard Eluate is composed of a mixture of a pulverised coal fly ash leachate and a MSWI fly ash leachate in a suitable mixing ratio. The eluate from coal fly ash provides oxyanions and the eluate from MSWI fly ash provides elevated metal concentrations.

The within laboratory variability or repeatability in the chemical analysis of the Standard Eluate is generally very good. The repeatability (s_r) is often within 4 %. As the concentration to be measured decreases the uncertainty increases, here up to about 12 %. The between laboratory variability or reproducibility (s_R) in the chemical analysis of the Standard Eluate is on average a factor 2.6 larger than the within laboratory variability, which is quite good for a European wide validation. The repeatability (s_R) is often within 10 % relative standard deviation.
A Standard Eluate such as applied here is a useful means of evaluating analytical performance in validating leaching tests, of which eluate analysis is an integral part.

In table II the performance characteristics of the Standard Eluate analyses for the individual elements are provided.

Table II *Standard Eluate Analysis Performance Data*

		Eluate Analysis Validation						Leaching Test Validation					
Element	Units	Labs	Values	Outl.	Mean	s_r %	s_R %	Labs	Values	Outl.	Mean	s_r %	s_R %
As	µg/l	3	7		10.9	112.8	130.3	13	26	2	0.93	6.7	102
Ba	µg/l	15	42	1	27.1	3.95	12.85	34	68	4	26.6	3.6	11
Be	µg/l	4	10		1.39	1.06	145.1						
B	mg/l							34	68	5	1.196	2.4	7.1
Cd	µg/l	14	42	6	365	2.01	8.09	36	72	2	357	2.1	7.1
Co	µg/l	9	27	3	5.85	7.21	9.3	25	50	3	6.00	11.4	21
Cr	µg/l	15	45	3	81.8	4.18	8.53	36	72	3	83.3	3	8.9
Cu	µg/l	10	30	5	7.66	14.98	16.75	25	50	2	6.17	11.2	26
Mo	µg/l	14	41	3	70.3	5.27	16.05	36	72	4	235	2.9	6.2
Ni	µg/l	11	32	3	13.3	6.23	17.22	29	58	2	13.2	11.9	27
P	mg/l	4	12		91.7	10.27	86.76						
Pb	µg/l	14	41	4	75.9	4.21	21.2	37	74		404	3.4	8.5
Sb	µg/l							31	62	6	6.56	20.3	30
SO4 as S	mg/l	9	27	3	50.5	1.48	7.62	28	56	1	52.0	2.8	11
V	µg/l	12	34	4	24.9	5.71	18.5	31	62	5	15.99	8.8	23
Zn	µg/l	16	47		18600	3.31	8.9	36	72	3	18134	2.8	6.7

If the repeatability is limited to 10 % then the following overall characteristics apply:

	Median	Min.	Max.
s_r %	2.9	2	9
s_R %	7.7	6	23

These values have been used as reference for the eluate analysis in EN 12457 1-4.

7. STATISTICAL EVALUATION OF EN 12457

In a European wide validation study according to ISO 5725-5, the performance characteristics of the compliance leaching tests EN 12457 1-4 for inorganic species were established. The uncertainty in the end result of a leaching test is composed of contributions from:

- the origin of the material (variation in production processes);
- the method of sampling in the field (differences in representativeness);
- the sample pretreatment (reduction of the field sample into laboratory sample(s) and preparation of the test portion from the laboratory sample before the leaching test);
- the leaching test itself and the experimental parameter variations as allowed by the tolerances;
- the chemical analysis (uncertainty in the determination of concentration in the eluates).

In the interlaboratory exercise to establish the uncertainty of the compliance leaching test, the contributions of the first two items listed above were not included. The validation covers all aspects from the receipt of the laboratory sample from the same primary field sample, onwards.

The validation was carried out with 12 - 14 European laboratories on seven types of waste materials. One of the wastes was tested according to all parts of EN 12457. The wastes selected for the validation were chosen such as to represent as broad a range of wastes as possible, as the standard is intended for general use on waste.

In the validation study the following starting points were used:
The laboratory samples were all taken from one large batch of the different wastes. To be representative for normal practice rigorous homogenisation of wastes (i.e by size reduction and

repeated mixing) was not applied. Only the normal primary sampling in the appropriate manner and the size reduction as needed were carried out. Only in the case of metallurgical slag a separate laboratory sample was provided to assess the difference between central and individual size reduction.

The experimental plan was designed by CEN/TC 292 WG 2 on the basis of each laboratory being given two laboratory samples of each waste to be tested. This is in accordance with ISO 5725-5 section 5 dedicated to heterogeneous material (such as for instance sand or aggregate samples to be tested). However, in order to verify that the variability due to the eluate analysis is not dominant, the laboratories participating in the validation were requested to perform a single complete leaching test on each laboratory sample and to analyse the eluates in duplicate.

The wastes examined cover all the grain size classes to which the compliance leaching test applies: powdered wastes and sludges (0 µm to about 125 µm), fine-grained materials (0 mm to 4 mm) and coarse-grained materials (0 mm to greater than 4 mm) after the required size reduction.

For the choice of waste and component, it was not intended to only investigate waste – component combinations for which already much experience with the leaching test has been obtained. Also some waste-component combinations were tested for which it can be expected that one or more of the requirements would not be easily fulfilled (for example heterogeneity in metallurgical slag, biological instability of sewage sludge). Such combinations were involved in the validation to also give insight in the potentially increased uncertainty for these matrices.

In the validation of the 4 parts of EN 12457, 3 clusters of labs were formed to share the workload of carrying out the testing of 7 wastes. Standard reporting sheets in Excel were developed to facilitate data processing.

In figure 2 and 3 examples are given of the robust statistics on respectively cobalt in contaminated soil (COS) using EN 12457-1 test data and lead in metalurgical slag (MES) using EN 12457-2 test data. From the duplicate analysis of all eluates the within laboratory variability of the analysis is given ($s_{r,Anal}$). For comparison the results of the analysis of the standard eluate and the results of the eluate analysis validation are given. From the duplicate extraction, the within laboratory variability of the test is obtained ($s_{r,test}$). The overall evaluation of participating labs provides the between laboratory variability (s_R). In case of Co in COS a relatively normal Z-score curve is obtained. However, in the case of Pb the heterogeneity of the metalurgical slag is illustrated by the steep slope in the Z-score curve. Even central size reduction to < 4 mm (MESr), which implies that potentially a more homogeneous material was shipped has not resulted in better reproducibility, which implies true heterogeneity in this material for Pb. For Sb, As and B an improvement in reproducibility is noted after central size reduction as compared to individual size reduction (particle size of shipped material: 0 - 40 mm). For comparison, the results of the percolation and pH dependence leaching test on COS respectively MESr are given. In addition, the performance of the analytical measurements on eluates (Eluate analysis validation, see paragraph 10) for the constituent shown is given as well (STE = Standard Eluate).

In figure 4 the within laboratory test variability ($s_{r,Test}$ %) is plotted against s_R (%). This gives two different linear relationships depending on the level of uncertainty. At within laboratory test uncertainties up to about 20 % a slope of about 2 – 2.5 is observed, which corresponds to the normal relationship between within and between lab variabilities in validation work. Beyond this point data may show a very high s_R (reproducibility) at a reasonable (low) $s_{r,Test}$ level. This is indicative of systematic errors leading to an off set in the concentration level (F in FCM, Cu in SBW). Theoretically at extreme heterogeneity the within laboratory variability and the between laboratory variability become equal. So equal and high within test and between lab variability on leaching test results in combination with low analytical uncertainty points at

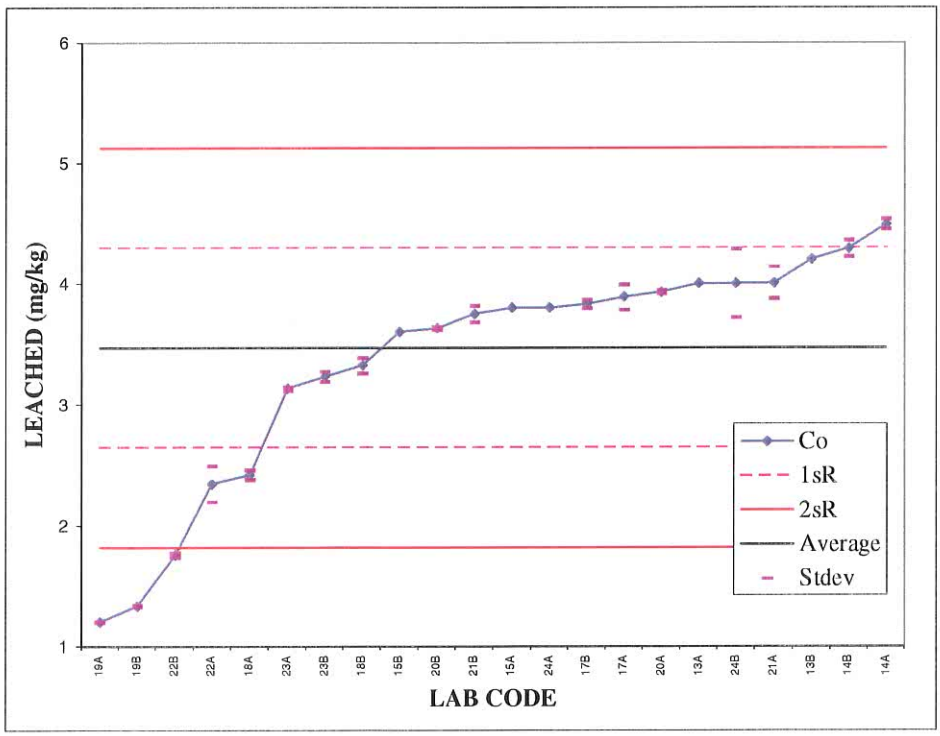
heterogeneity for a specific component. This type of relationship can be observed for "heterogeneous" materials. However, a waste may be homogeneous for some and heterogeneous for other constituents. It may also be heterogeneous for composition and homogeneous in leaching. For instance, Pb in MSWI bottom ash is heterogeneous in Pb composition, but it is homogeneous in Mg. Also Cu is heterogeneous in composition and much more homogeneous in leaching.

Some observations relate to specific materials properties. In case of sewage sludge the biological activity affects the results in the validation work (NH4, TOC, SO4). Already in the ruggedness evaluation sensitivity to this factor was noted. It implies that the turn-around time for testing and analysis needs to be kept as short as possible. In view of the observed gas formation (H_2) in the testing of SBW reducing the head space volume is not good. It is more important to have a constant head space. In the text of the standards a note on potential gas formation is needed to make the user aware, that under certain circumstances gas formation may occur at proper measures shall be taken to prevent too high pressure build up.

The aspect of sample hetereogeneity in waste samples is an inherent issue, which needs to be factored in when leaching data are used for decision making and judgements of acceptability.

Since the repeatability and reproducibility on a range of elements in four materials is good, the conclusion is that the leaching test as such is suitable and provides adequate results, provided the condition of sufficient level of sample homogeneity is fulfilled. To improve overall performance of the tests emphasis must be placed on means to minimize the effects of sample heterogeneity on repeatability and reproducibility. A possible option to reach this goal is to apply further size reduction and to deal with the possibly increased leachability relative to field conditions in another manner.

Sample	COS	Average	3.45	mg/kg	Sr Anal	0.05	mg/kg	1.5	%		%
Test	EN 12457-1	STD	0.83	mg/kg	Sr Test	0.21	mg/kg	6.2	%	rtest	17.4
No labs	11				SR	0.83	mg/kg	25	%	R	70.8



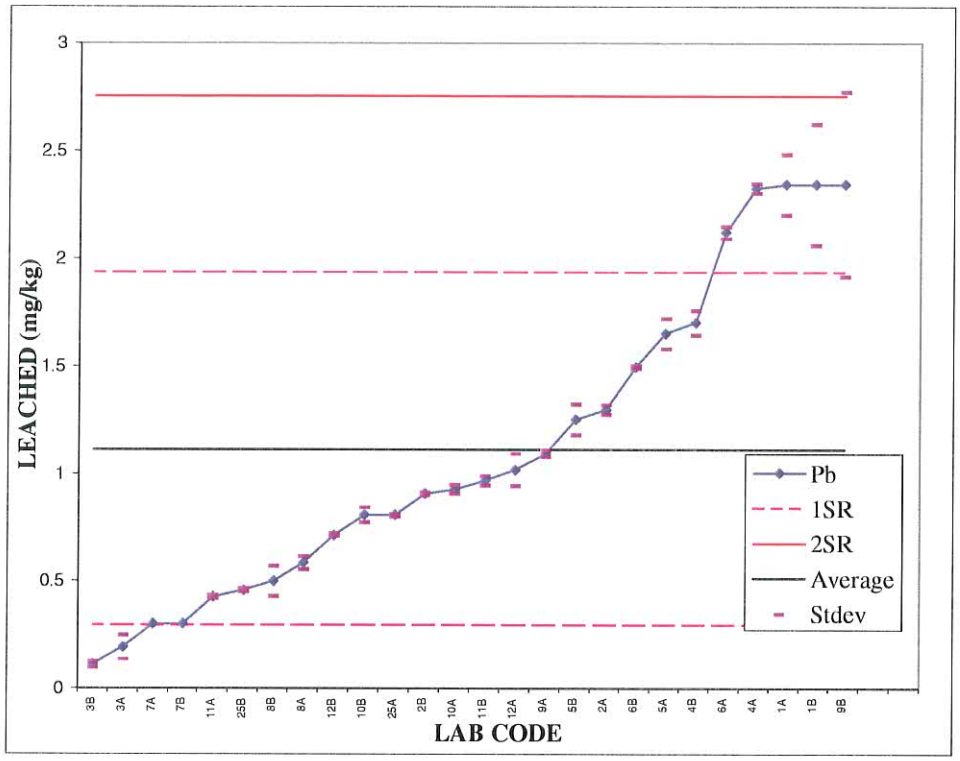
Percolation test	mg/kg
L/S=1	3.7

STE	
Conc. (mg/l)	0.006
Sr Anal(%)	11.4
SR Anal(%)	22

Eluate analysis val.	
Conc. (mg/l)	0.0744
Sr Anal(%)	1.9
Conc. (mg/l)	5.85
Sr Anal(%)	7.21

Figure 2 Robust statistics applied on Co leaching from contaminated soil (COS) using EN 12457-1.

Sample	MESr	Average	1.20	mg/kg	Sr Anal	0.049	mg/kg	4.4	%		%
Test	EN 12457-2	STD	0.82	mg/kg	Sr Test	0.37	mg/kg	31.1	%	rtest	87
No labs	13				SR	0.97	mg/kg	81	%	R	227



Percolation test

	mg/kg
L/S=10	0.16

pH stat (own pH)

L/S=10	mg/kg
pH 8.5	0.054

STE

Conc. (mg/l)	0.404
Sr Anal(%)	3.4
SR Anal(%)	8

Figure 3 Robust statistics applied on Pb leaching from metalurgical slag (MES size reduced) using EN 12457-2

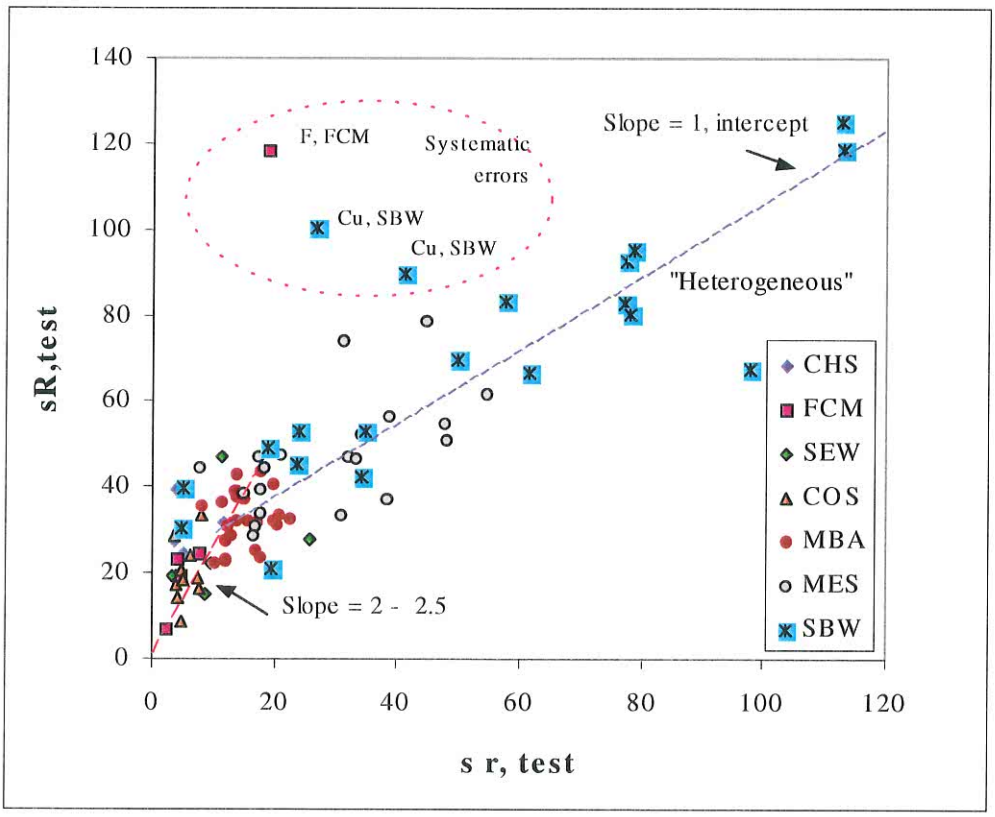


Figure 4. Plot of the within laboratory test variability ($s_{r,test}$) against the between laboratory variability (s_R).

8. ANALYTICAL PERFORMANCE EVALUATION

For the wide range of solutions analysed by any analytical laboratory it is very difficult to assess matrix interferences on individual eluates. The manner of data presentation as shown in figure 5 based on incidental duplicate analysis in the regular performance of analysis on a wide range of solutions allows to generate an instrument performance characteristic. This allows interferences to be identified fairly easily and also allows a better assessment of realistic limits of determination and limits of detection. Any point well to the right or above the cluster of data points is suspect of either sample heterogeneity or interferences. When concern arises that heterogeneity or interferences may play a role a duplicate analysis plotted in a graph like this can provide information on the occurence of such an increased uncertainty in the analytical determination. Data points well outside the curve are suspect. Further evaluation of this type of data seems useful for internal laboratory quality control.

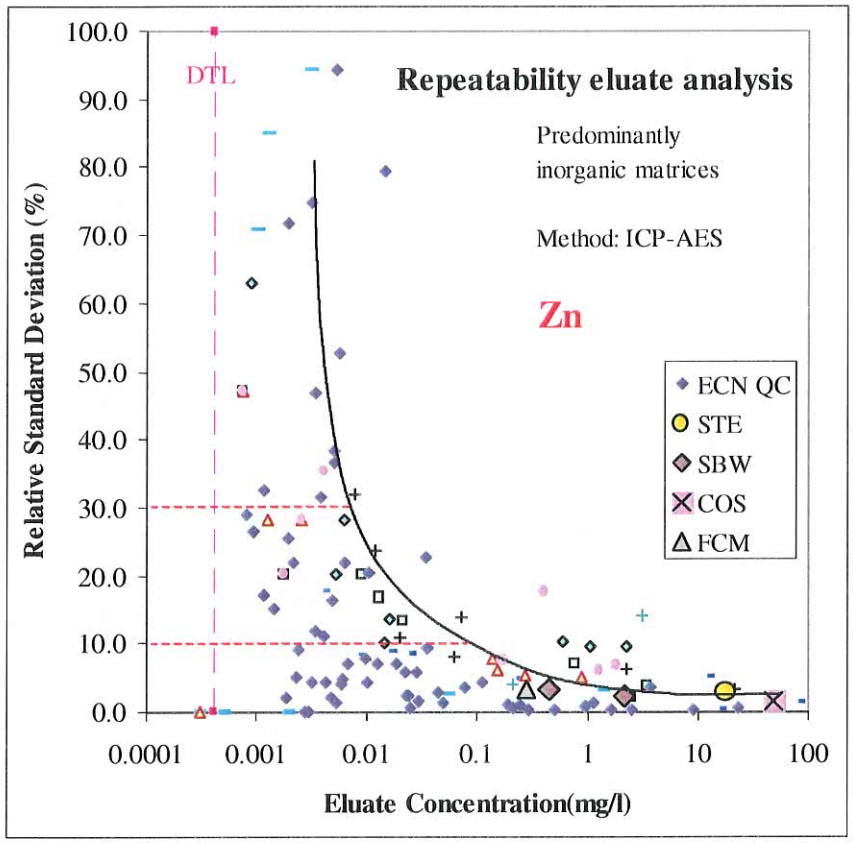


Figure 5. Analytical performance data for ICP based on duplicate analysis of Zn in eluates. (STE=standard eluate; SBW, COS and FCM are codes for the wastes studied; 5 year ECN QC data from wide range of eluates included for comparison).

9. EN 12457 1- 4 PERFORMANCE CHARACTERISTICS

Based on the outcome of the validation, performance characteristics for the parts of EN 12457 1- 4 have been derived. The statistical evaluation was conducted according to ISO 5725-5 section 6 providing "robust methods for data analysis": The average values, the repeatability standard deviation ($s_{r\ test}$) and the reproducibility standard deviation (s_R) were obtained. In order to compare and contrast the contribution of the analysis of the eluate to the overall uncertainty in the leaching test, Table III lists the repeatability standard deviation for the eluate analysis $s_{r,anal}$ as obtained in the validation study.

The repeatability is determined as an interval around a measurement result (i.e. "repeatability limit"). This interval corresponds to the maximum difference that can be expected (with a 95% statistical confidence) between one test result and another, both test results being obtained under the following conditions: the tests are performed in accordance with all the requirements of the present standard by the same laboratory using its own facilities and testing laboratory samples obtained from the same primary field sample and prepared under identical procedures. The repeatability limit was calculated using the relationship: $r_{test} = f\sqrt{2} * s_{r,test}$ with the critical range factor f = 2. For instance, for the first line of table III, the repeatability limit around a measurement result of 4,69 mg As/kg is ± 0,49 mg As/kg (i.e. ±10,4 % of 4,69).
The statistical evaluation of section 6 of ISO 5725-5 relies, among others, on two basic principles:

- a quasi normal distribution for the differences calculated for each pair of results : this is not generally the case in the validation program.
- an assumption that the extreme results are given by "poor quality" laboratories and, consequently, the robust method calculates the repeatability and the reproducibility on the basis of the "good quality" laboratories without being influenced by the results of the "poor quality" laboratories. In addition it is assumed that the group of such extreme values is not too important.

However in the case of heterogeneous materials, the concept of a distinction between "poor" and "good" laboratories includes not only the quality of operation of the laboratory in accordance with the applied standardised method, but also the heterogeneity between the laboratory samples. The consequence is that each and every laboratory has the same chance of receiving a laboratory sample that produces extreme results.

Table III. Example results of the validation studies of EN 12457-2

EN 12457-2			Repeatability standard deviation	Reproducibility standard deviation	Repeatability limit (comparing two measurements)	Reproducibility limit (comparing two measurements)	Number of labs	Eluate analysis repeatability standard deviation
Sample	Element	Average						
Code		mg/kg	$s_{r,test}$ %	s_R %	r_{test} %	R %	N	$s_{r,anal}$ % [3]
COS	As	4.69	3.7	29.3	10.4	82.0	11	3.4
COS	Pb	33.19	4.9	7.4	13.7	20.7	11	3.4
COS	Cd	19.71	3.9	16.6	10.9	46.5	11	4.1
COS	Ni	4.70	4.1	14.7	11.5	41.2	11	3.1
COS	Co	4.31	5.0	19.0	14.0	53.2	11	4.1
Sample	Element	mg/kg	$s_{r,test}$ %	s_R %	r_{test} %	R %	N	$s_{r,anal}$ % [3]
MBA	Mo	0.48	17.7	26.7	50	75	12	7.3
MBA	Sb	0.29	19.1	36.0	53	101	12	5.5
MBA	SO_4	1517	15.6	39.6	44	111	14	3.9
MBA	Ba	1.62	11.9	37.0	33	104	13	2.6
MBA	Cu	4.57	18.3	22.8	51	64	14	1.8
Sample	Element	mg/kg	$s_{r,test}$ %	s_R %	r_{test} %	R %	N	$s_{r,anal}$ % [3]
MESr [1,2,4])	As	0.047	38.4	39.7	108	111	10	10
MESr [2])	Sb	0.76	30.9	34.9	87	98	13	2.2
MESr	Ba	6.20	8.4	26.1	24	73	13	1.9
MESr	B	1.96	15.3	31.0	43	87	12	3.6
MESr [2])	Pb	1.20	31.1	81.2	87	227	13	4.4

[1] Too poor analytical data [2] Obvious heterogeneity (low $s_{r,Anal}$, very high and/or equal $s_{r,Test}$ and s_R) [3] The repeatability standard deviation of the eluate analysis as obtained in the validation of EN 12457 is consistent with the repeatability standard deviation obtained in the eluate analysis validation study. [4]) MESr – sample size reduced centrally by the sample dispatching laboratory as opposed to size reduction by participating laboratories according to the standard.

Based on the overall evaluation table IV gives the resulting typical values for repeatability and reproducibility limits as well as their observed ranges. The typical value is derived from

the data in table III by taking the median value and eliminating data as indicated in table III and rounding the numbers.

Table IV *Typical values and observed ranges of the repeatability and reproducibility limits*

Results of the validation of the compliance leaching test EN 12457- 2	Typical value	Observed range
r repeatability limit	24 %	7 % - 100 %
R reproducibility limit	72 %	20 % - 160 %

In figure 6 the analytical repeatability ($s_{r,anal}$), and test repeatability ($s_{r,test}$) are shown in relation to the test reproducibility (s_R) for all materials tested using EN 12457 Part 2. This illustrates the relative contribution of the individual steps.

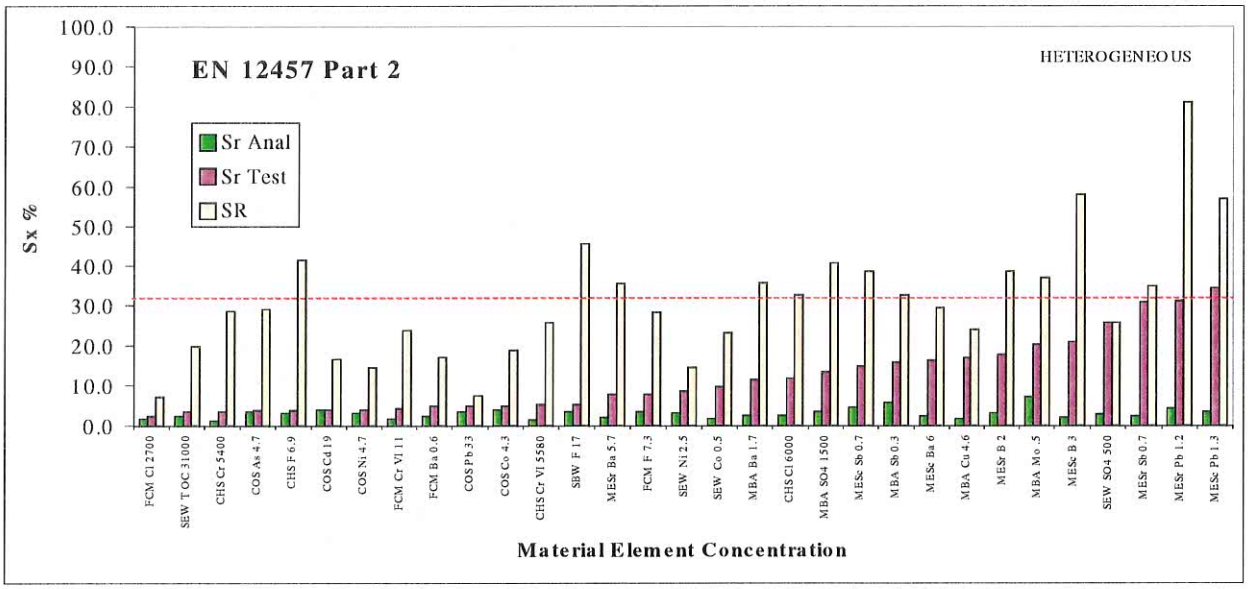


Figure 6. Analytical repeatability, test repeatability and reproducibility of EN 12457 Part 2. (Labels reflect Material code – element - leached amount; dotted line reflects the average reproducibility standard deviation).

10. ELUATE ANALYSIS METHODS VALIDATION

Within the European standardisation committee CEN/TC292 "Characterisation of Waste" two standards were developed for the analysis of waste eluates on the basis of existing international and European standards for the determination of the corresponding parameters in water: prEN 13370: Determination of Ammonium-N, AOX, conductivity, Hg, phenol index, TOC, CN- easy liberatable, F- and ENV 12506: Determination of pH, As, Cd, Cr(VI), Cu, Ni, Pb, Zn, Cl-, NO2-, SO4-. These standards are urgently needed as important tools for controlling limit values in waste eluates as regulated by the European Landfill Directive. For this purpose they need to be validated. After some difficulty sufficient laboratories were found who were willing to take part in the validation exercise.

The overall statistics of the interlaboratory study on validation of methods for eluate analysis, (prEN 13370/ENV 12506) for a selection of parameters out of the range of eluates prepared (COS, FFC, SEW, SBW, SYN1, SYN2, SYN3), are given in table V. More than 90% of the calculated relative repeatabilities are below 10%, whereas about 75% of the reproducibilities are below 40%. These results indicate that most of the tested analytical procedures can be used with

adequate precision for the determination of relevant parameters in waste eluates. Bad reproducibilities were probably caused by concentration levels near the determination limit (e.g. NO3-, Ion Chromatography, ISO 10304, FFC, SEW), high concentrations of interfering substances in the eluates (e.g. CN-, Photometry, ISO 6703, SEW) or insufficient quality of some of the participating laboratories in performing the analysis (e.g. Pb, AAS, ISO 8288, SYN1, SYN2).

Table V *Results of the in the interlaboratory study on validation of methods for eluate analysis (prEN 13370/ENV 12506) – Contaminated Soil Eluate (COS), Filtercake Eluate (FCM), Sand blasting waste eluate (SBW) and Synthetic eluate (Syn3.)*

Parameter	Material Code	Standard	Units	Number of			Mean	s_r	s_R
				Labs	Values	Outliers		[%]	[%]
As - ICP	COS	ISO 11885	µg/l	11	33	3	20.6	4.76	28.1
As - Hydride AAS	COS	EN 11969	µg/l	13	39	-	17.4	5.32	33.9
As - Hydride AAS	SEW	EN 11969	µg/l	12	36	6	15.2	5.2	51.4
As - ICP	SEW	ISO 11885	µg/l	11	33	6	139	7.66	19.4
As - ICP	Syn3	ISO 11885	µg/l	3	7	-	10.9	113	130
F - Electrode	FCM	ISO 10359	mg/l	7	21	6	0.71	3.25	12.2
F – IC	FCM	ISO 10304	mg/l	7	20	4	0.63	1.35	19.5
F - Electrode	SBW	ISO 10359	mg/l	10	30	-	7.66	0.78	12.9
F - IC	SBW	ISO 10304	mg/l	11	33	-	7.42	2.06	16.6

Figures 7, 8 and 9 contain examples of the graphical presentation of the results of the the interlaboratory study on validation of methods for eluate analysis as cited in prEN 13370 and ENV 12506. The figures allow the evaluation of the reproducibilities of the analytical procedures in the investigated real waste and synthetic eluates (Figure 5 and 6) and a comparison of the performance of different methods for the same parameter (figure 7). Here As and F are shown. In case of As, a significant difference is noted for ICP versus the generally more sensitive hydride AAS method. This is attributed to the complex eluate of sewage sludge leachate, where ICP due to the high flame temperature leads to additional destruction of the sample during analysis, which is lacking in the hydride method.

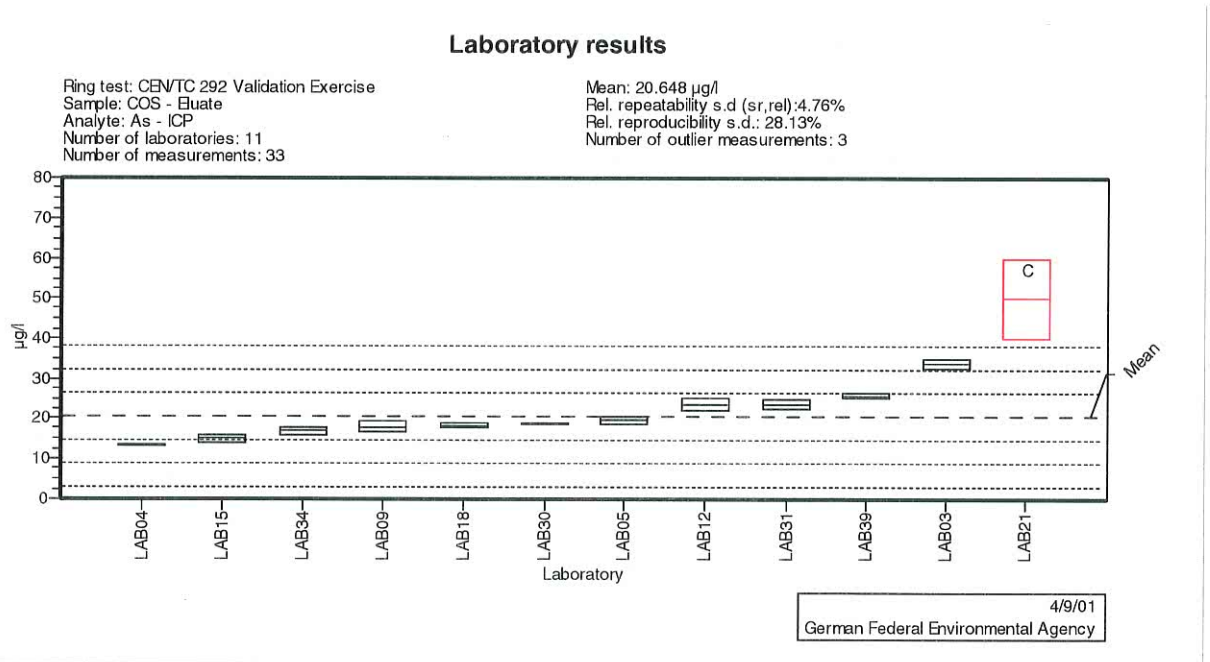


Figure 7. Evaluation of the repeatability and reproducibilities of the analytical procedures of As by ICP in COS eluate. (C means rejected based on too large within lab variability)

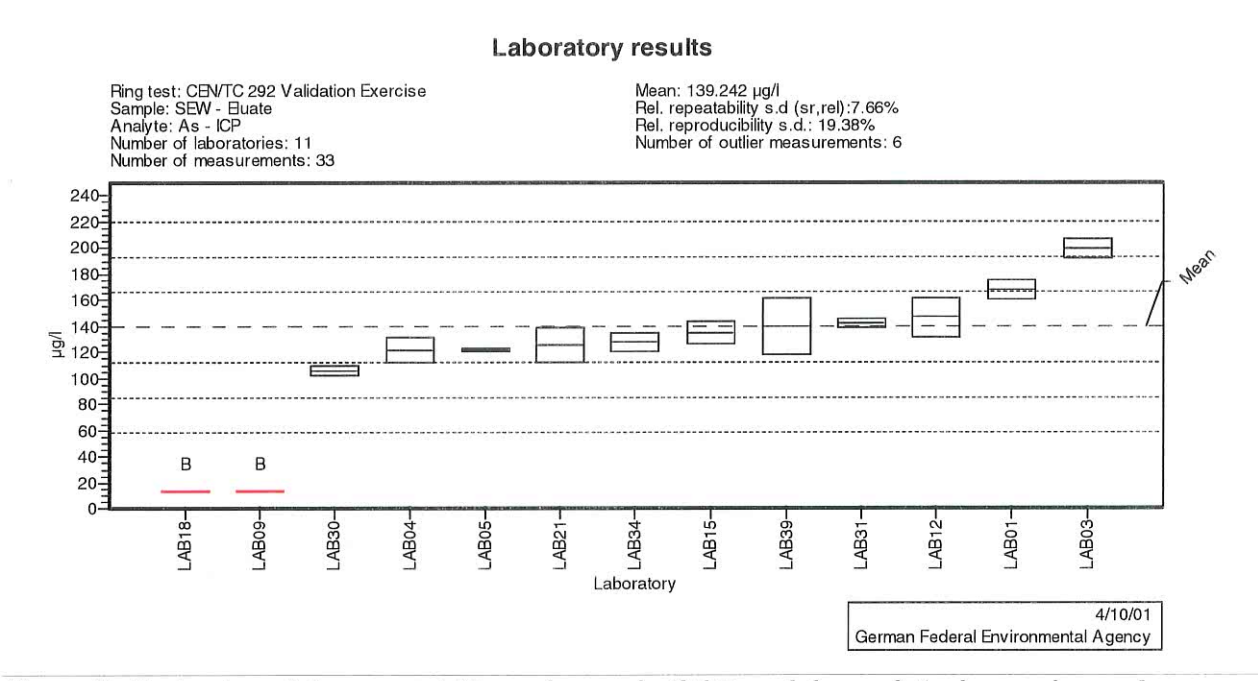


Figure 8 Evaluation of the repeatability and reproducibilities of the analytical procedures of As by ICP in SBW eluate. (B denotes rejected values).

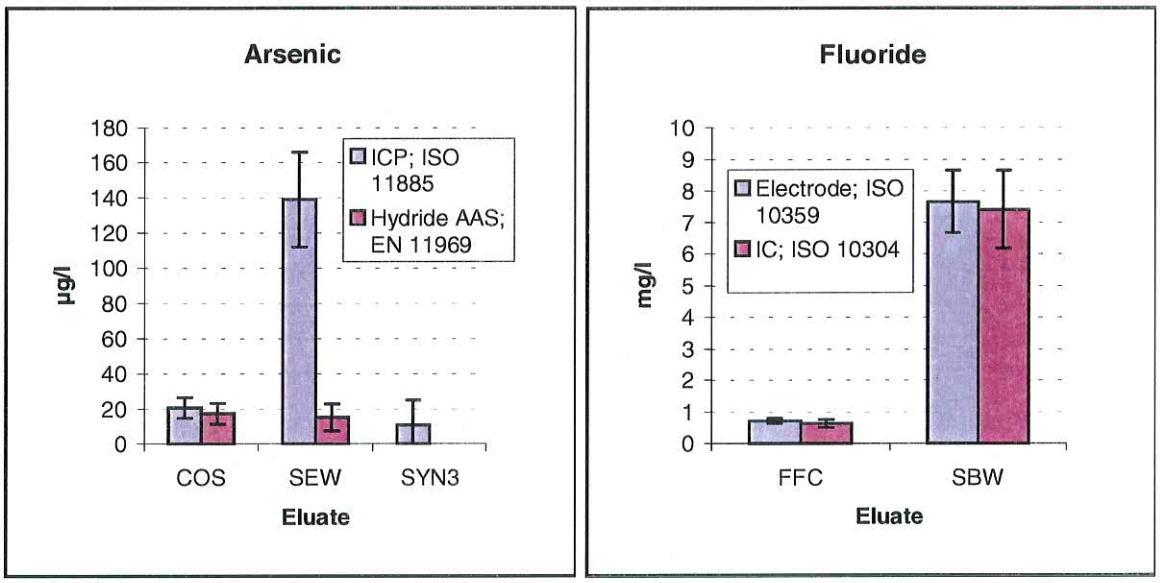


Figure 9. Examples of the comparison of different methods for the same parameter.

11. ELUATE ANALYSIS PERFORMANCE

The data from the validation of PREN 12506 have been assessed according to ISO 5725-2. In table VI the tested parameter (here As), the accepted combination of method, parameter and sample, and the results and statistics are shown.
The acceptance criterion was:

- Minimum number of laboratories: 6
- Minimum number of results (outliers excluded): 18

Table VI. Results of the in the interlaboratory study on validation of methods for eluate analysis for As in different matrices.

Parameter	Matrix	Standard	Units	Number of					Mean	s_r	s_R	S_r *	S_R *
				Labs total	Labs accepted	Values total	Values accepted	Outliers				%	%
As - Hydride AAS	COS	EN ISO 11969	µg/l	13	13	39	39	-	17.4	0,92	5,90	5.32	33.9
As – ICP	COS	EN ISO 11885	µg/l	12	11	36	33	3	20.6	0,98	5,79	4.76	28.1
As – ICP	SEW	EN ISO 11885	µg/l	13	11	39	33	6	139	10,6	26,9	7.7	19.4

* S_r relative repeatability; S_R relative reproducibility

The validation of this standard was performed on a selection of waste and synthetic eluates. For some parameters different analytical methods were validated. For most methods validation data are available for at least two eluates per parameter. In the case of As (EN ISO 11969), NO_2 (EN ISO 10304-1, EN ISO 10304-2 and EN ISO 13395) and V (EN ISO 11885) only one matrix was validated. In any case, for the analyses of a given parameter within a specific matrix, it is the responsibility of the laboratory to choose the appropriate analytical method depending on the expected interference and concentration range as mentioned in the according standards.

The data from the validation of PREN 13370 have been assessed according to ISO 5725-2. In table VII the tested parameter (here F), the accepted combination of method, parameter and sample, and the results and statistics are given. The acceptance criterion was the same as stated above

Table VII. Results of the in the interlaboratory study on validation of methods for eluate analysis (prEN 13370) for F in different matrices.

Parameter	Matrix	Standard	Units	Number of					Mean	s_r	s_R	S_r	S_R
				Labs total	Labs accepted	Values total	Values accepted	Outliers				%	%
F - Electrode	SBW	ISO10359-1	mg/l	10	10	30	30	-	7.66	0,060	0,99	0.78	12.9
F - IC	SBW	EN ISO 10304-1	mg/l	11	11	33	33	-	7.42	0,153	1,23	2.06	16.6
F - Electrode	FCM	ISO 10359-1	mg/l	9	9	27	21	6	0.709	0,023	0,086	3.25	12.2
F – IC	FCM	EN ISO 10304-1	mg/l	8	7	24	20	4	0.629	0,0085	0,123	1.35	19.5

The validation of this standard was performed on a selection of waste and synthetic eluates. For some parameters different analytical methods were validated. For some methods validation data are available for at least two eluates per parameter. In the case of Hg (EN 1483), CN- (ISO 6703-2, ISO/FDIS 14403), phenol index (ISO 6439, ISO/FDIS 14402) only one matrix was validated. For the analyses of a given parameter within a specific matrix, it is the responsibility of the laboratory to choose the appropriate analytical method depending on the expected interference and concentration range as mentioned in the according standards.

There is no international standard on equivalence testing between alternative physical or chemical methods available. However based on the F-test and the t-test for means (used are the s_R values) there is a realistic chance to prove equivalence between a number of method/matrix combinations.

12. CONTRIBUTORS AND PARTICIPANTS

The validation study was carried out with financial support from: - the European Commission DG Environment; Umwelt Bundes Amt – Berlin Germany; Bundesministerium für Land- und Forestwirtschaft, Umwelt und Wasserwirtschaft – Austria; Danish Environmental Protection Agency and Centre for Waste Research – Denmark; Ministry of Housing, Spatial Planning and the Environment – The Netherlands; Environmental Services Association Research Trust – United Kingdom; ADEME – France and Openbare Afvalstoffen Maatschappij voor het Vlaamse Gewest – Belgium. In the validation of EN 12457, 36 European laboratories from 11 EU member states and from Norway, Switzerland and Hungary participated. In the eluate analysis validation 40 European laboratories from EU member states and from the Czech Republic participated.

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