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STUDY REPORT

Comparison of dissolution methods of metals in sediments and sludges

This document is issued for information and is based on results and observations from proficiency tests of A.G.L.A.E.

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ABSTRACT

Deviations between dissolution methods are frequently observed in AGLAE's proficiency tests for aluminium, chromium and nickel in sediments and aluminium, chromium and potassium in sludges. We have studied for these metals deviations between dissolution methods during our PTs since 2010 and we gathered the methods as follows: "partial" methods, "total" methods and the *aqua regia* method (HNO_3/HCl) in a closed system with microwave heating.
Whatever the parameter or the matrix, "total" methods give higher results than the method HNO_3/HCl in a close system with microwave heating which also gives higher results than "partial" results.
In sediments, the most significant deviations are observed for aluminium: average deviations observed between "partial" and "total" methods for Al are 108% versus 34% for Cr and 18% for Ni.
In sludges, the most significant deviations are observed for potassium: between the method HNO_3/HCl in a closed system with microwave heating and the "partial" methods, average deviations observed are 28% for K versus 20% for Al and 7,4% for Cr.

Deviations have been studied by linking them to three factors: the concentration level, the content of total organic carbon (TOC) and the type of matrix (sludge or sediment).
For sediments, the concentration level could impact the deviations observed for Al: deviations are more significant for low concentration levels.
For sludges, concentration level has an impact on deviations for Al and Cr: deviations are also more significant for low concentration levels.
For sediments, the content in TOC doesn't seem to impact deviations observed for Cr or Al. For sludges, there is a correlation between the content in TOC and deviations observed.
Finally, it seems that the importance of the deviations between methods is different when the analysis is carried out in sludges or in sediments. Deviations observed in sediments are more significant than in sludges.

TABLE OF CONTENTS

PRESENTATION AND COMMENTS

TABLES

TABLE OF GRAPHS

1. INTRODUCTION

AGLAE has been providing proficiency tests for more than 15 years about metals in solid matrices.
Deviations between results of laboratories are frequently observed according to the dissolution method carried out: “total” dissolution method (hydrofluoric/perchloric etching, alkali fusion…), “partial” dissolution methods (*aqua regia* with different types of heating).

The purpose of this study report is to quantify and interpret these deviations. This study has been carried out on several metals for which we frequently observe deviations and on methods the most used by laboratories, and in two types of solid matrices: sediments and sludges.

In order to analyse the deviations observed, results of proficiency tests of several years have been studied. The different dissolution methods have been gathered in three groups:

- “Total” dissolution methods: hydrofluoric/perchloric etching, alkali fusions.
- “Partial” dissolution methods: HCl/HNO_3 under reflux, boiling HCl/HNO_3 in a glass tube, HCl/HNO_3 in a heating block
- HCl/HNO_3 in a closed system with microwave heating

Important note

In this study, when we mention deviations between dissolution methods, these are deviations between the means of results of laboratories which carried out different dissolution methods.
The fact that these deviations come from digestion methods is the most probable hypothesis, even if one needs to be careful with hidden sources of bias. However, we checked that deviations observed were not due to the analytical technique carried out.

2. DATA

Metals in solid matrices are provided by AGLAE in three programmes:

- Programme 9: « Chemical analysis and metals in sediments »
- Programme 40: « Chemical analysis and metals in recoverable sewage sludges »
- Programme 43: « Chemical analysis and metals in contaminated sites and soils »

The study was carried out particularly on metals which present the most frequently deviations between methods.
So, a summary of deviations between dissolution methods observed in these three matrices since 2010 has been made, ie 14 and 15 proficiency tests for programme 9 and 40 (2 tests by campaign) and 6 proficiency tests for programme 43 (1 test by campaign).

	Frequency of significant deviations between dissolution method by programme		
Parameter	Programme 40 Sludges (15 PTs)	Programme 9 Sediments (14 PTs)	Programme 43 Soils (6 PTs)
Al	8	14	1
As	2	2	0
Ca	2	0	0
Co	2	0	0
Cr	4	12	0
K	9	0	0
Mg	4	0	0
Na	4	0	0
Ni	1	6	0
Pb	1	1	0
Zn	0	1	0

Table 1: Frequency of significant deviations between dissolution methods by programme

Table 1 shows that in soils, only one deviation between dissolution methods for Al in 6 tests is observed. That’s the reason why mineralization of metals in soils was not studied in this report.

However, for sediments (programme 9), deviations are almost systematically observed for Al and Cr. For Ni, deviations are observed for a little less than half of tests.
So, for sediments, deviations between dissolution methods have been studied for Al, Cr and Ni.

For sludges (programme 40), the number of deviations observed is more important for Al and K with an occurrence of about 1 test out of 2. For Cr, Mg and Na, deviations are regularly observed the same occurrence. Nevertheless only one of the three parameters is included in this study; the choice was Cr in order to make comparisons with sediments.
Thus, in sludges, deviations between mineralization methods have been studied for Al, Cr and K.

2.1. DESCRIPTION OF PROFICIENCY TESTS

For programme 9, the type of matrix is sediment. It can be sediments from ports, a marine sediment or a river sediment. In order to have materials homogeneous enough for usage in our tests, sediments are dried, crushed and sieved at 150µm or 80µm (see table 2). Each test gathers around 40 participants.

Test[1]	Matrix	Treatment
16M9.2	Sediment from ports	Dried, crushed and sieved at 150µm
16M9.1	Marine sediment	Dried, crushed and sieved at 150µm
15M9.2	Sediment from ports	Dried, crushed and sieved at 150µm
15M9.1	Sediment from ports	Dried, crushed and sieved at 150µm
14M9.2	River sediment	Dried, crushed and sieved at 150µm
14M9.1	Sediment from ports	Dried, crushed and sieved at 150µm
13M9.2	River sediment	Dried, crushed and sieved at 150µm
13M9.1	Marine sediment	Dried, crushed and sieved at 150µm
12M9.2	River sediment	Dried, crushed and sieved at 150µm
12M9.1	River sediment	Dried, crushed and sieved at 150µm
11M9.2	River sediment	Dried, crushed and sieved at 80µm
11M9.1	River sediment	Dried, crushed and sieved at 80µm
10M9.2	River sediment	Dried, crushed and sieved at 80µm
10M9.1	River sediment	Dried, crushed and sieved at 80µm

Table 2: Type of matrix used for programme 9

Results are expressed by referring to the mass of dry matter. It is asked to laboratories to determine the content of dry matter of the material at (105 ± 5)°C in compliance with the NF ISO 11465 (94) standard or any other effective standard during the test.

For the programme 40, the type of matrix is sludge. It can be a mix of sludges, a sludge from urban waste water treatment plant (urban WWTP), an industrial sludge, a sludge from washing station or a dredged sludge. Sludges are also dried, crushed and sieved at 150µm or 80µm (see table 3). Each test gathers around 40 participants.

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[1] For example the test 13M9.2 corresponds to the second test of programme 9 from campaign 2013 ; the test 16M40.1 corresponds to the first test of programme 40 from campaign 2016

Test	Matrix	Treatment
17M40.1	Mix of sludges	Dried, crushed and sieved at 150µm
16M40.2	Mix of sludges	Dried, crushed and sieved at 150µm
16M40.1	Sludge from urban WWTP	Dried, crushed and sieved at 150µm
15M40.2	Sludge from urban WWTP	Dried, crushed and sieved at 150µm
15M40.1	Sludge from washing station	Dried, crushed and sieved at 150µm
14M40.2	Mix of sludges	Dried, crushed and sieved at 150µm
14M40.1	Industrial sludge	Dried, crushed and sieved at 150µm
13M40.2	Sludge from urban WWTP	Dried, crushed and sieved at 150µm
13M40.1	Sludge from urban WWTP	Dried, crushed and sieved at 150µm
12M40.2	Sludge from urban WWTP	Dried, crushed and sieved at 150µm
12M40.1	Sludge from urban WWTP	Dried, crushed and sieved at 150µm
11M40.2	Dredged sludge	Dried, crushed and sieved at 80µm
11M40.1	Industrial sludge	Dried, crushed and sieved at 80µm
10M40.2	Industrial sludge	Dried, crushed and sieved at 80µm
10M40.1	Sludge from urban WWTP	Dried, crushed and sieved at 80µm

Table 3: Type de matrix used for programme 40

Results are expressed by referring to the mass of dry matter. It is asked to laboratories to determine the content of dry matter of the material at (105 ± 5)°C in compliance with the NF EN 12880 (2000) standard or any other effective standard during the test.

Sediments and sludges used for our tests are naturally contaminated (no artificial enrichment in metals by spiking). Concentration ranges studied are described in the table 4 below:

	Concentration range	
Parameter	Sediments (Programme 9)	Sludges (Programme 40)
Al (g/kg of dry matter)	14-54	7-55
Cr (mg/kg of dry matter)	20-255	45-24000
Ni (mg/kg of dry matter)	10-37	-
K (g/kg of dry matter)	-	1,2-7,5

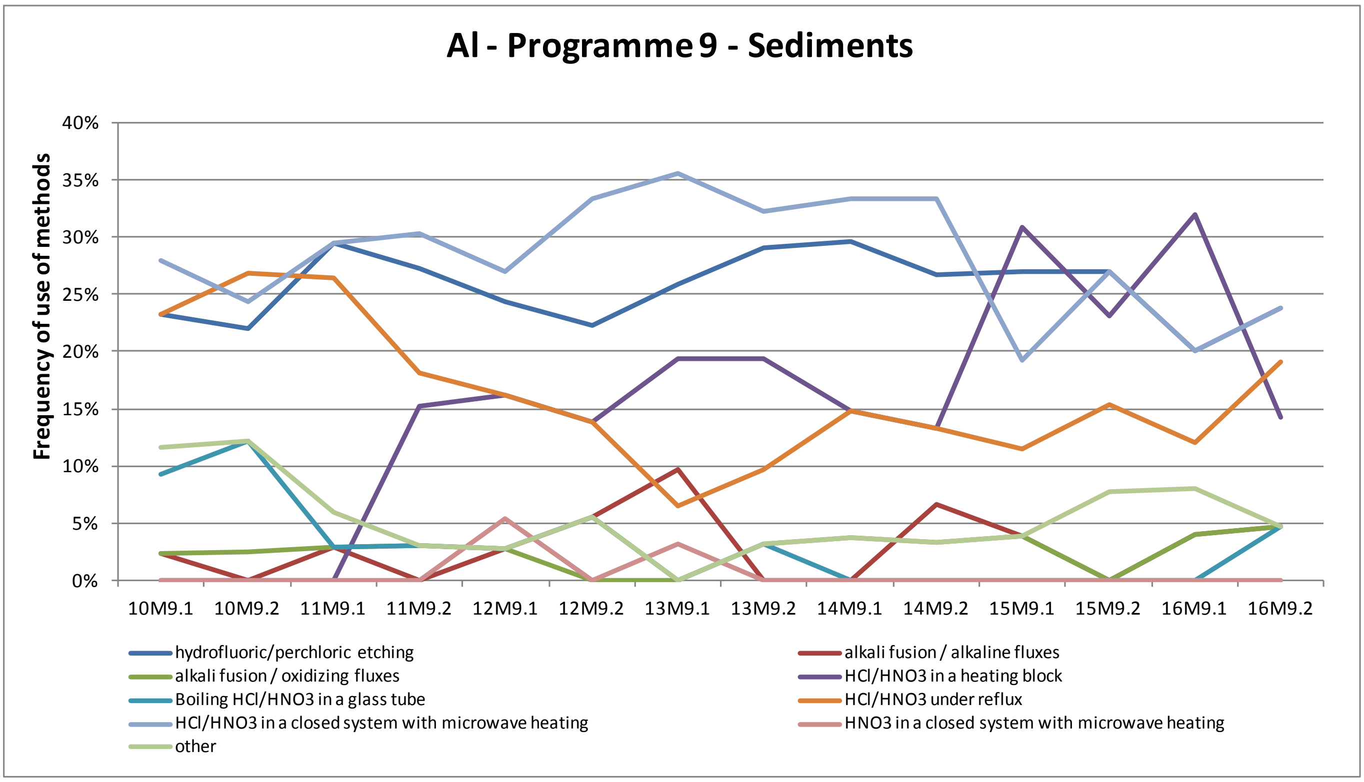
Table 4: Concentration range of metals

2.2. DISSOLUTION METHODS

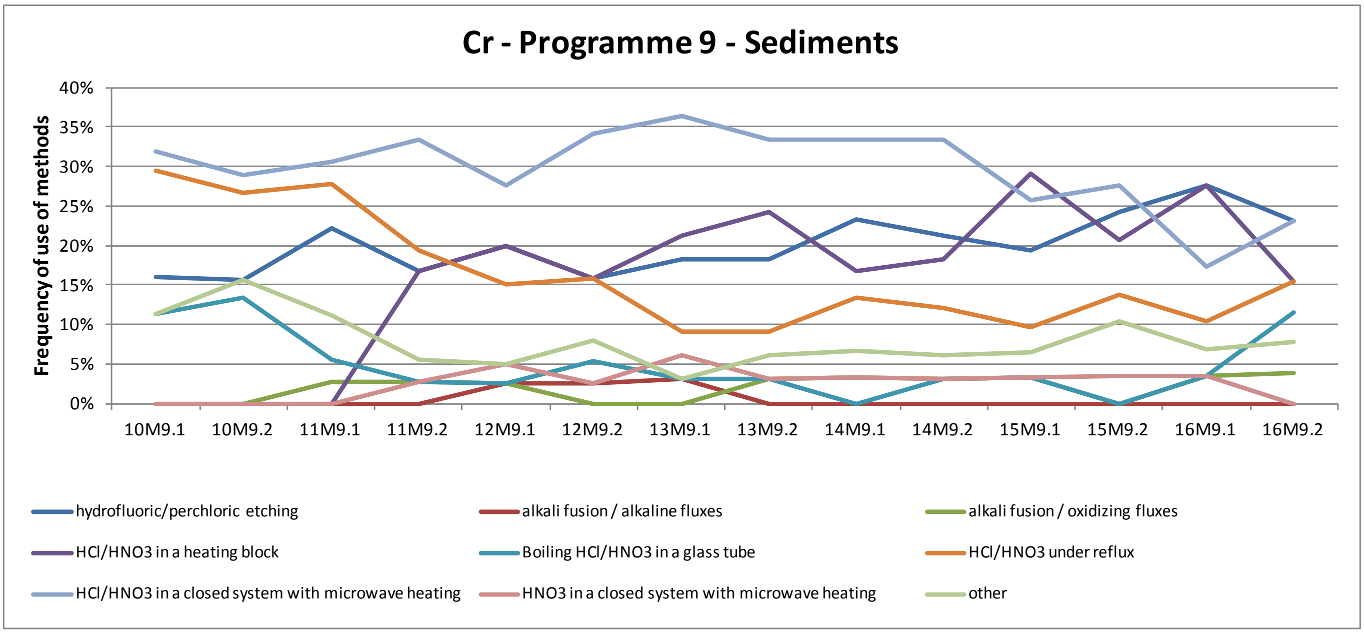
For each test, participants can specify their dissolution methods. Thus, we can highlight potential deviations between methods or it enables us to treat separately data if several populations of results are statistically highlighted. These data allow us to know which methods are used by laboratories and to monitor the evolutions of technique over time.

The following graphs show the frequency of use of several dissolution methods (graphs 1, 2, 3, 4, 5 and 6) in the tests since 2010. Thus, we can see if methods have progressively been set aside in favor of other methods.

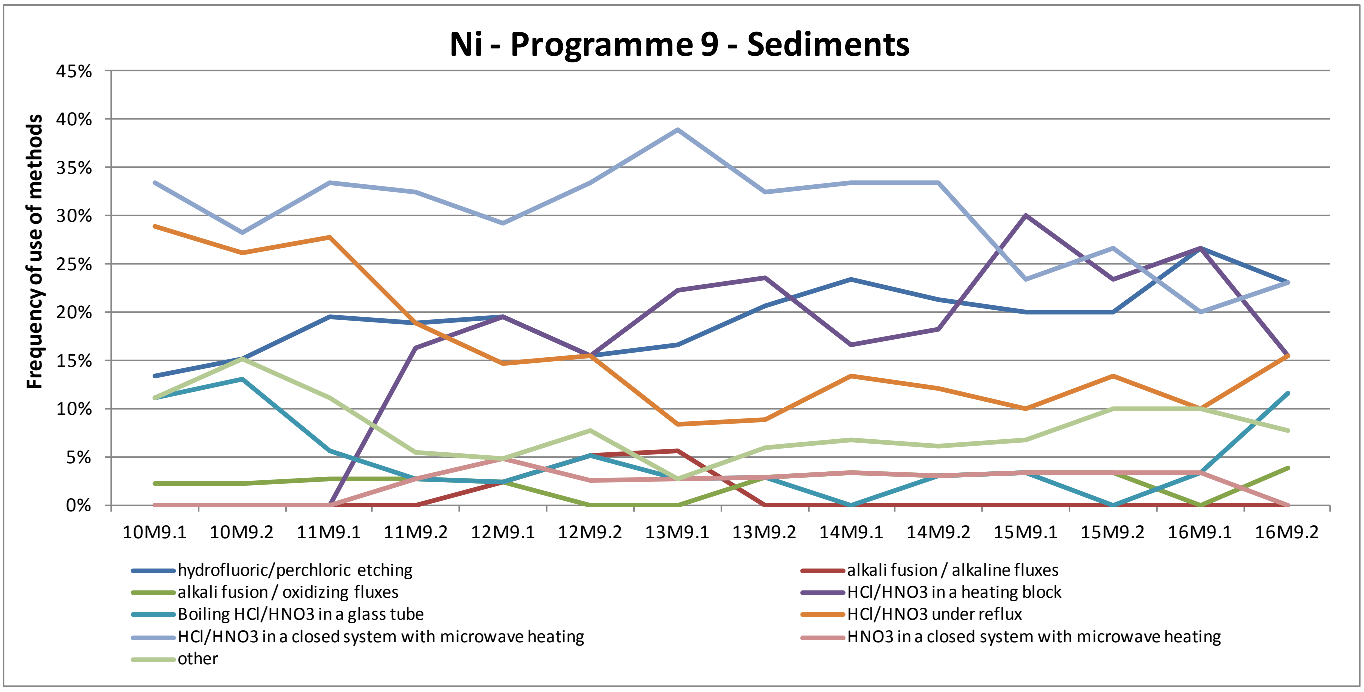
Sediments - Programme 9



Graph 1: Dissolution methods of Al in sediments



Graph 2: Dissolution methods of Cr in sediments



Graph 3: Dissolution methods of Cr in sediments

For sediments (programme 9), the most used dissolution methods are:

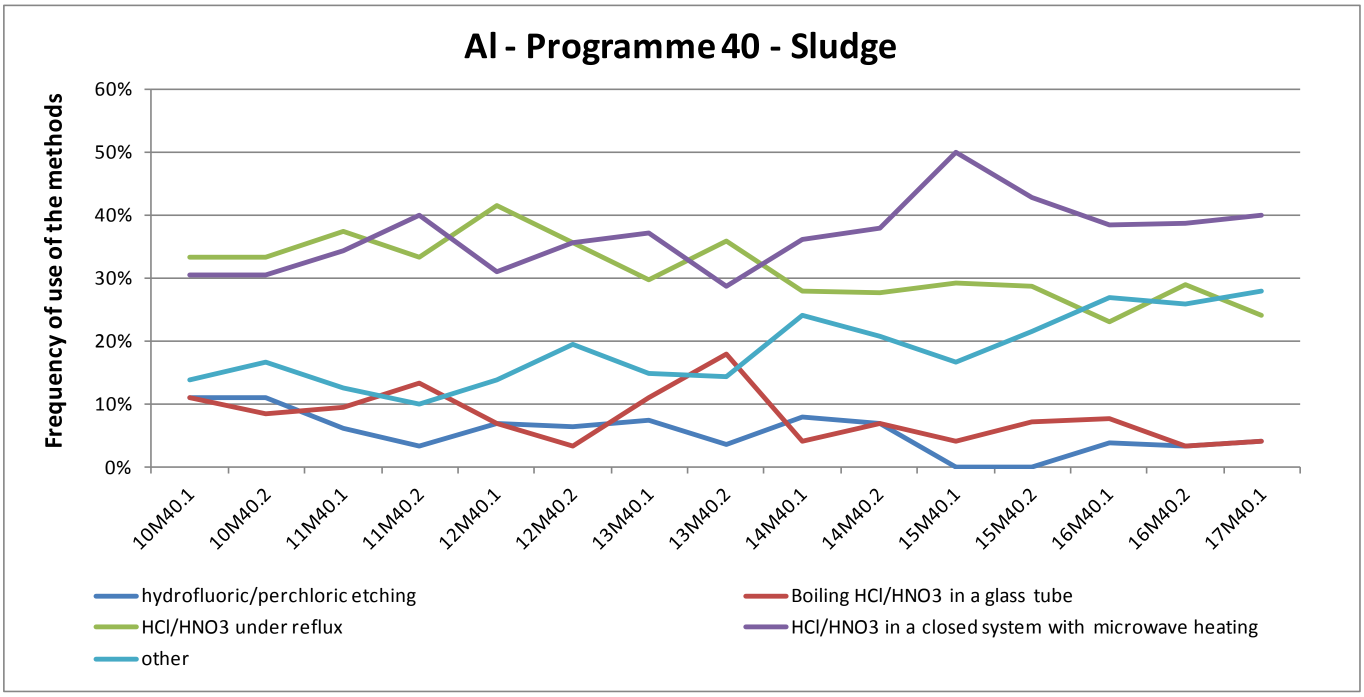
- hydrofluoric/perchloric etching (median 22%),
- HCl/HNO_3 in a heating block (median 17%),
- HCl/HNO_3 under reflux (median 15%),
- HCl/HNO_3 in a closed system with microwave heating (median 30%).

The method with heating block which appeared in 2011 in our test, replaced in part the methods with boiling heating and under reflux.

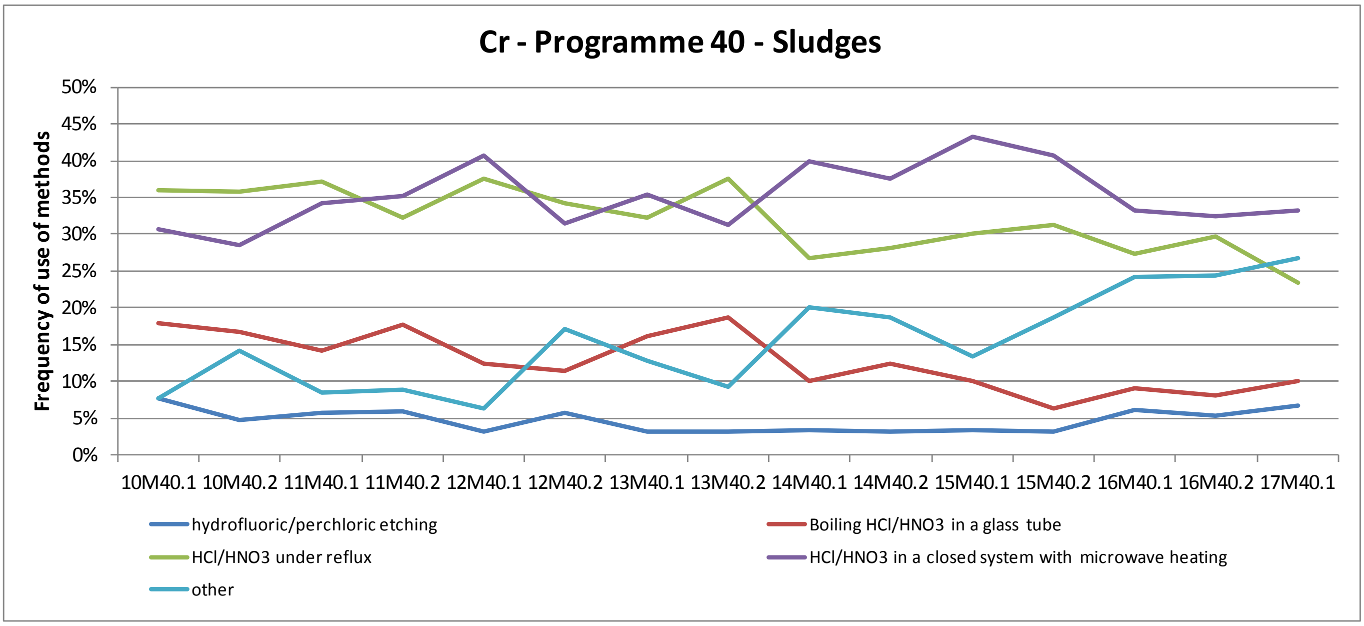
In order to gather some methods, deviations between methods have been studied since 2010. Thus, it appears that during our tests the deviations between methods were mainly between 3 groups of methods. So, in this report we studied methods gathered like in our tests:

Method A: HCl/HNO_3 in a closed system with microwave heating
Method B: HCl/HNO_3 under reflux, HCl/HNO_3 in a heating block and Boiling HCl/HNO_3 in a glass tube
Method C: hydrofluoric/perchloric etching, alkali fusion / alkaline fluxes, alkali fusion / oxidizing fluxes

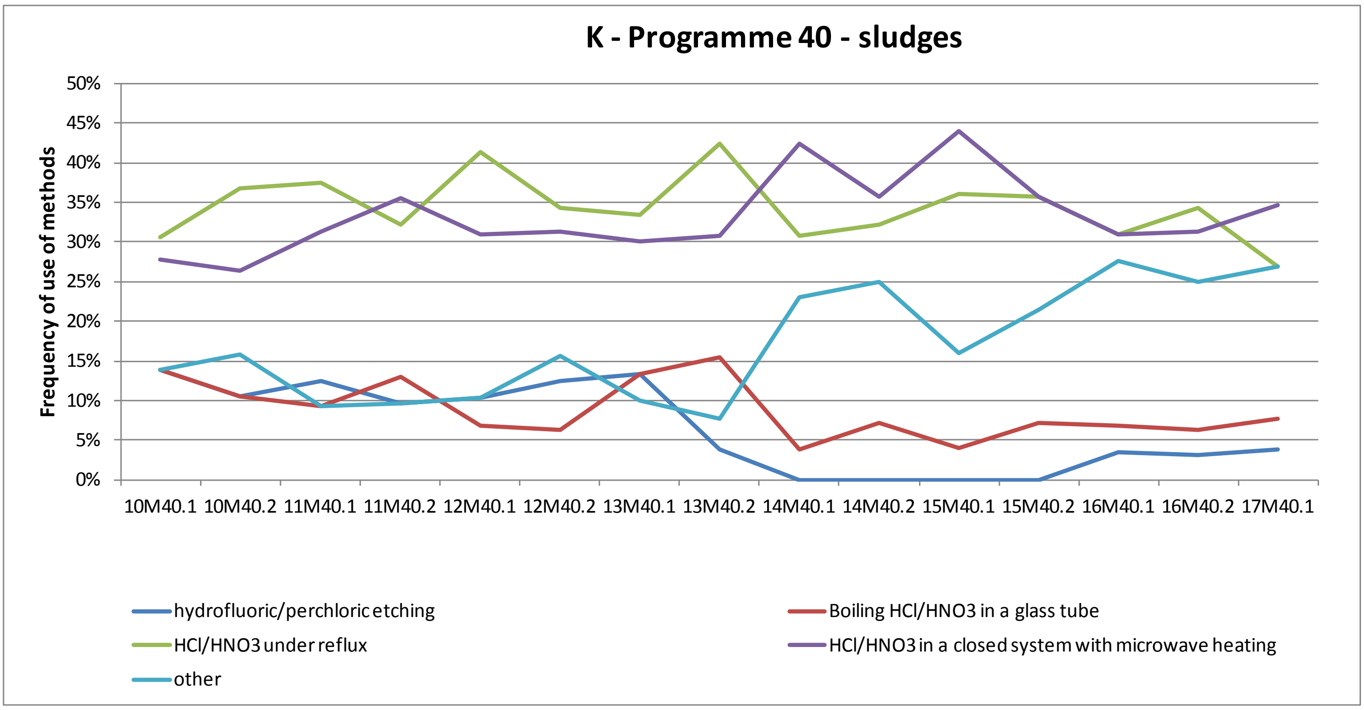
Sludges - Programme 40



Graph 4: Dissolution methods of Al in sludges



Graph 5: Dissolution methods of Cr in sludges



Graph 6: Dissolution methods of K in sludges

For sludges (programme 40), the most used dissolution methods are:

- HCl/HNO_3 under reflux (median 32%),
- HCl/HNO_3 in a closed system with microwave heating (median 35%).

Note that more and more "other" methods are used (median 16%), gathering for example dissolution methods HCl/HNO_3 closed tube graphite block, HCl/HNO_3 on heating plate, boiling HCl/HNO_3 in a plastic tube… These “other” methods even though they represent around 25% of methods used for example in 17M40.1 test, they individually represent few laboratories (<8 laboratories per test).

However, unlike what we observed in sediments, hydrofluoric/perchloric etching is practically not used in sludge (median of 6% against 22% in sediments). Furthermore, this method is less and less used as seen with K for example in sludge: from 2014, this method is practically not used anymore.

For sludge also, in order to gather some methods, the deviations between methods observed in tests carried out since 2010 have been studied. Thus, it appears that deviations between methods are separated mainly between 2 groups of methods. So, in this report we studied methods gathered like in our tests:

Method A: HCl/HNO_3 in a closed system with microwave heating
Method B: HCl/HNO_3 under reflux and Boiling HCl/HNO_3 in a glass tube

Table 5 below describes the dissolution methods studied in this document:

	Sediments (programme 9)	Sludges (programme 40)
Method A	• HCl/HNO_3 in a closed system with microwave heating	• HCl/HNO_3 in a closed system with microwave heating
Method B	• HCl/HNO_3 under reflux, • HCl/HNO_3 in a heating block • Boiling HCl/HNO_3 in a glass tube	• HCl/HNO_3 under reflux, • Boiling HCl/HNO_3 in a glass tube
Method C	• hydrofluoric/perchloric etching, • alkali fusion / alkaline fluxes, • alkali fusion / oxidizing fluxes	–

Table 5: Summary of dissolution methods

Methods A and B are considered identical in sludges and sediments even if in sludges for method A, HCl/HNO_3 in a heating block method is not represented.

2.3. ANALYTICAL STANDARD AND COMPARISON OF METHODS

The following table presents a non-exhaustive list of standards available for dissolution method the most used by laboratories in sediments and sludges.

Dissolution method	Normative reference
HCl/HNO_3 under reflux	NF ISO 11466 NF EN 13346 NF EN 16174
HCl/HNO_3 in a heating block	NF ISO 11466
Boiling HCl/HNO_3 in a glass tube	NF EN 13346
HCl/HNO_3 in a closed system with microwave heating	NF ISO 12914 NF EN 13346 NF EN 16174
hydrofluoric/perchloric etching	NF X 31-147 NF ISO 14869-1
alkali fusion / alkaline fluxes, alkali fusion / oxidizing fluxes	NF ISO 14869-2

Table 6: Non-exhaustive list of current standard

NF X 31-147, NF ISO 14869-1 and NF ISO 14869-2 standards indicate that hydrofluoric/perchloric etching and alkali fusion are “total” dissolution methods.
In most of other standard using *aqua regia*, it is indicated that *aqua regia* digestion doesn’t always lead to a total decomposition of the sample.
Thus, *aqua regia* dissolution methods, whatever the heating mode used, are considered as “partial”.

3. DEVIATIONS BETWEEN DISSOLUTION METHODS

3.1. DATA TREATMENT

Results of interlaboratory tests have been treated method by method with the same statistical tools than in our proficiency tests. Means and standard deviations were calculated with robust calculation algorithms from all participants’ results (modified version of algorithm A and S from ISO 13528 standard).
Thus, for each parameter and each test, a mean by method (m) is obtained. The mean of the means of each method (M) is also calculated for each test. In order to overcome issues of concentration level from a test to another or from a parameter to another, the relative mean (m/M) of each method is calculated. An example is given below (table 7).

PT	Parameter	Unit	Mean by method (m)	Mean of all means (M)	Relative Mean m/M
16M9.1	Al Method A	g/kg of dry matter	25,327	32,318	0,78
	Al Method B		16,783		0,52
	Al Method C		54,845		1,70
14M40.2	Cr Method A	mg/kg of dry matter	17,555	15,8025818	1,11
	Cr Method B		14,050		0,89

Table 7: example of calculation of the relative mean

Method A: HCl/HNO_3 in a closed system with microwave heating; Method B: HCl/HNO_3 under reflux or in a heating block (programme 9) or Boiling HCl/HNO_3 in a glass tube; Method C: hydrofluoric/perchloric etching, alkali fusion / alkaline fluxes, alkali fusion / oxidizing fluxes.

Methods can be compared overcoming any scale issue. Thus, in the example above for 16M9.1 test, results of method C are on average higher than results of methods A and B because the relative mean of method C is superior to 1.

3.2. STATISTICAL TREATMENT

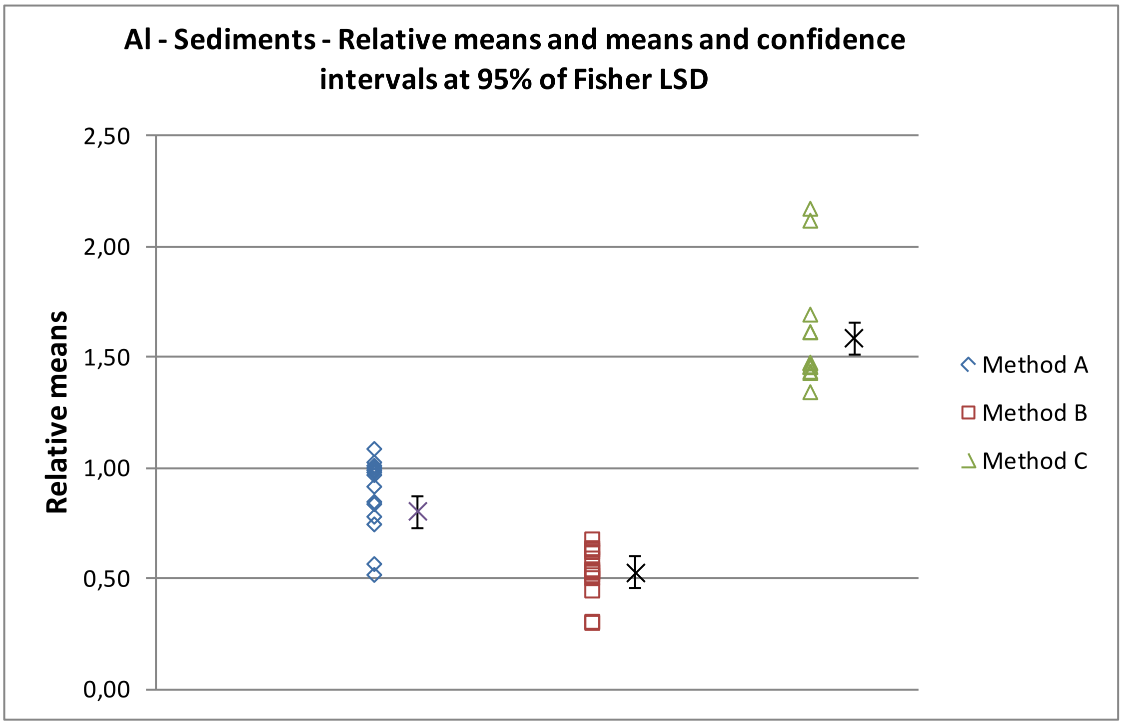
Relative means calculated for each chosen parameter and for each test were treated with an analysis of variance. This treatment allows testing the significance of deviations between relative means of each method. Calculation were made using Statgraphics® software after checking homoscedasticity of variance (homogeneity of variance from a mineralization method to another) and the normality of the relative means for each method.

First, the sediments (programme 9) will be studied then the sludges (programme 40) before comparing our observations in a third part.

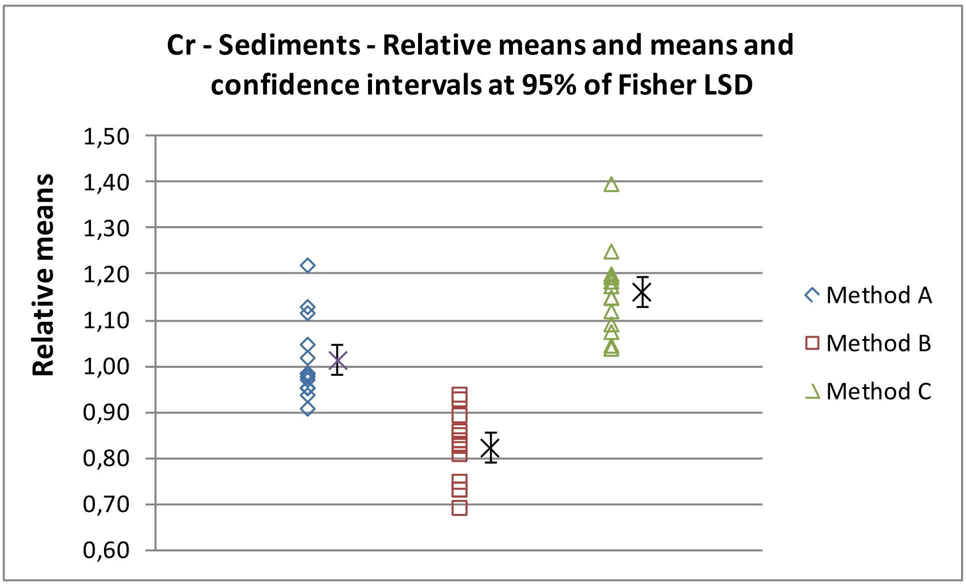
Sediments - Programme 9

Relative means

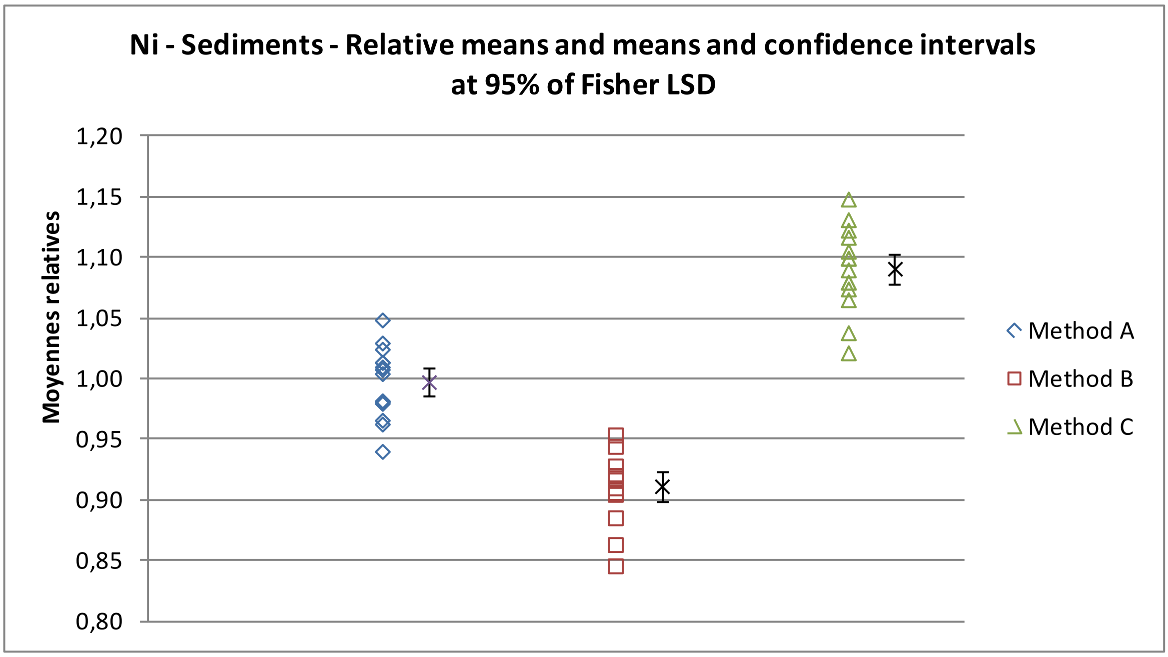
Graphs below (graphs 7, 8 and 9) present the relative means and the means and confidence intervals at 95% of Fisher LSD obtained in sediments for Al, Cr and Ni, for each method. They enable to check if deviations are significant at error risk of 5%. A deviation is significant if the confidence intervals (vertical bars) don’t overlap.



Graph 7: Distribution of relative means and significance of deviations of Al in sediments



Graph 8: Distribution of relative means and significance of deviations of Cr in sediments



Graph 9: Distribution of relative means and significance of deviations of Ni in sediments

Method A: HCl/HNO_3 in a closed system with microwave heating; Method B: HCl/HNO_3 under reflux or in a heating block (programme 9) or Boiling HCl/HNO_3 in a glass tube; Method C: hydrofluoric/perchloric etching, alkali fusion / alkaline fluxes, alkali fusion / oxidizing fluxes.

For Al, Cr and Ni, deviations between results obtained with dissolution methods A, B or C are significant, confidence intervals don't overlap.

Furthermore, whatever the parameter is, the highest results are found for method C ("total" dissolution method); extractions with *aqua regia* (methods A and B) give lower results. Nevertheless, method A gives intermediate results between methods B and C.

In the table below (table 8) are presented the mean deviations of relative means between each method and each parameter.

	Mean deviation observed between relative means		
Parameter	Methods A and B	Methods A and C	Methods B and C
Al	35%	71%	106%
Cr	19%	15%	34%
Ni	8,5%	9,3%	18%

Table 8: Mean deviations observed between the relative means in sediments

Al presents the highest mean deviations between methods, Ni the smallest.

For the 3 metals, the highest deviations are between methods B and C.

Maximum and minimum deviations of relative means observed during our test between each method and for each parameter have been studied (table 9).

	Deviations observed between relative means					
	Methods A and B		Methods A and C		Method Bs and C	
Parameter	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum
Al	11%	64%	31%	165%	72%	187%
Cr	4,9%	49%	3,3%	49%	14%	70%
Ni	12%	20%	0,29%	19%	6,8%	26%

Table 9: Minimum and maximum deviations between relative means in sediments

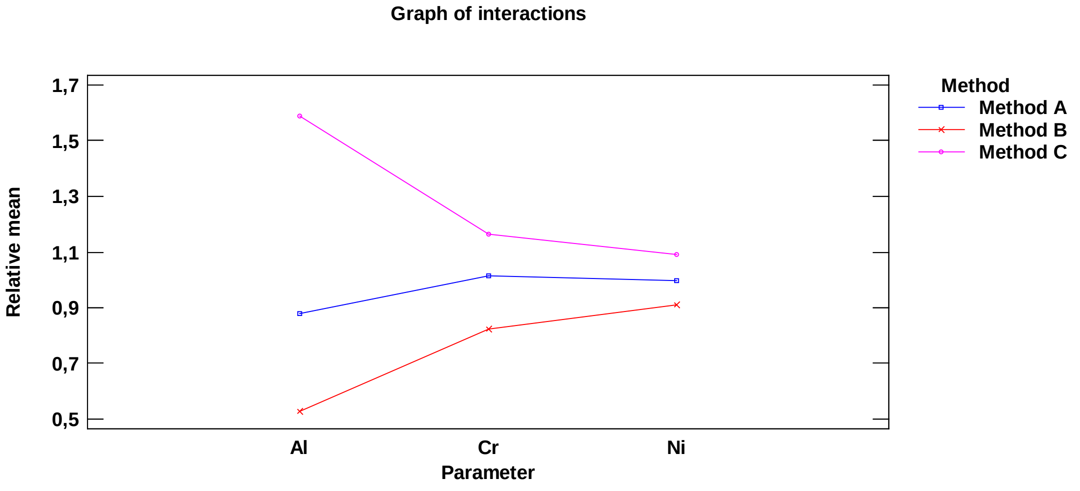
The biggest maximum and minimum deviations are obtained for Al. For the three metals, the biggest minimum and maximum deviations are also between methods B and C.

After analysing the relative means as a function of the parameter and the method with an analysis of variance (table 10), we can see that they significantly vary depending on the method (probability inferior to 0,01). Furthermore, the effect is also variable from a parameter to another (probability of the interactions of factors parameters/methods inferior to 0,01), i.e. that deviations between methods are not that much high from a parameter to another.

Analysis of variance for relative mean

Source	*Sum of squares*	*Df*	*Mean square*	*F-ratio*	*P-value*
MAIN EFFECTS					
A:Parameter	0	2	0	0,00	1,0000
B:Method	5,90372	2	2,95186	202,49	0,0000
INTERACTIONS					
AB	3,3115	4	0,827874	56,79	0,0000
RESIDUAL	1,7056	117	0,0145778		
TOTAL (CORRECTED)	10,9208	125			

Table 10: Analysis of variance for sediments



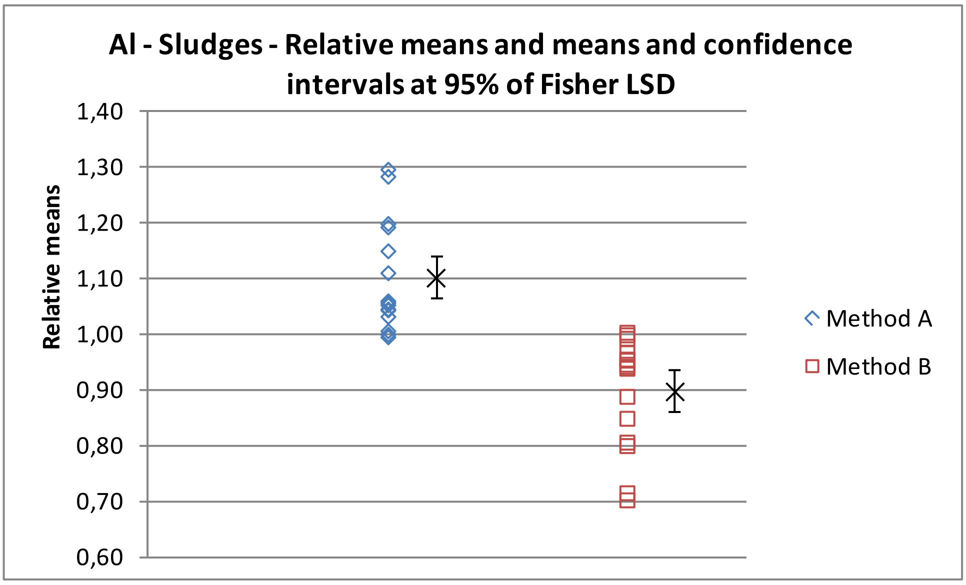
Graph 10: Graph of interactions in sediments

The graph above (graph 10) confirms the previous observations; Al is the parameter with the biggest deviations between methods. Cr presents also bigger deviations than Ni. Furthermore, method C always gives the highest results, followed by method A and method B whatever the parameter is.

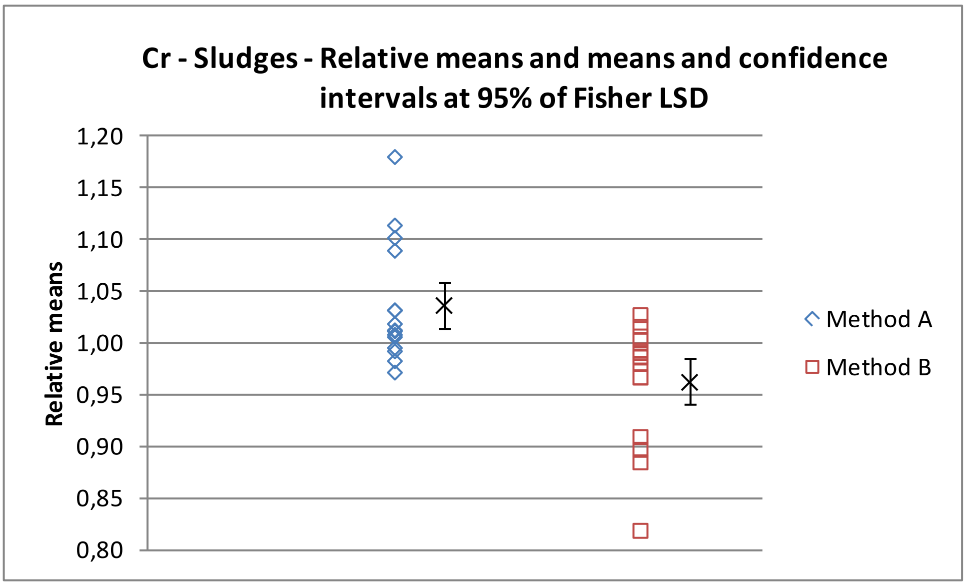
Sludges – Programme 40

Relative means

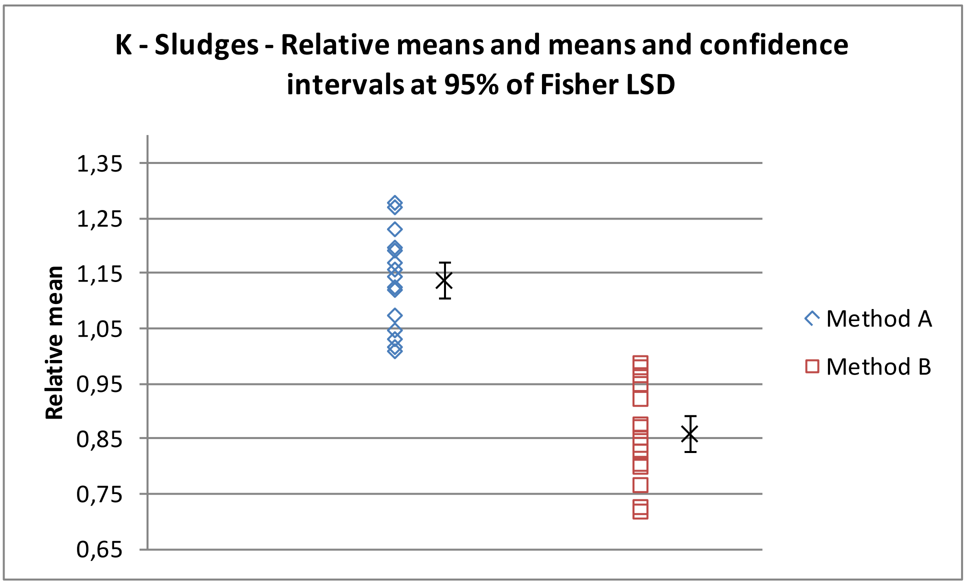
Graphs below (graphs 11, 12 and 13) presents the relative means and the means and confidence intervals at 95% of Fisher LSD obtained in sediments for Al, Cr and K, for each method. They allow checking if deviations are significant at error risk of 5%. A deviation is significant if the confidence intervals (vertical bar) don't overlap.



Graph 11: Distribution of relative means and significance of deviations of Al in sludges



Graph 12: Distribution of relative means and significance of deviations of Cr in sludges



Graph 13: Distribution of relative means and significance of deviations of K in sludges
Method A: HCl/HNO_3 in a closed system with microwave heating; Method B: HCl/HNO_3 under reflux or Boiling HCl/HNO_3 in a glass tube

For Al, Cr and K, deviations between results obtained with dissolution methods A and B are significant, confidence intervals don't overlap.
Furthermore, like in sediments, with an extraction with *aqua regia*, the microwave heating (method A) gives higher results than the other type of heating.

In the table below (table 11), the mean deviations of relative means between each method for each parameter are presented.

Parameter	Mean deviations between relative means of methods A and B
Al	20%
Cr	7,4%
K	28%

Table 11: Mean deviations observed between relative means in sludges.

K has the most significant mean deviations between methods, Cr the lowest.

Table 12 below presents maximum and minimum deviations of relative means observed during the tests between each method and for each parameter.

	Deviations observed between relative means of methods A and B	
Parameter	Minimum	Maximum
Al	0,11%	59%
Cr	0,79%	36%
K	2,2%	56%

Table 12: Minimum and maximum deviations observed between relative means in sludges

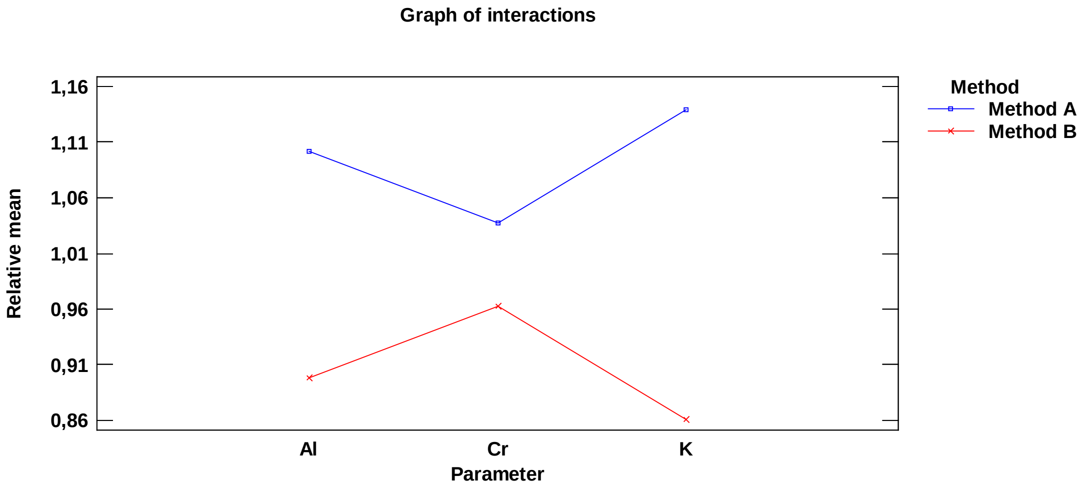
K and Al present similar maximum deviations and they are higher than Cr. The most significant are obtained for Al.

After analysing the relative means as a function of the parameter and the method with an analysis of variance (table 13), we can see that they significantly vary depending on the method (probability inferior to 0,01). Furthermore, the effect is also variable from a parameter to another (probability of the interactions of factors parameters/methods inferior to 0,01).

Analysis of variance for relative mean

Source	*Sum of squares*	*Df*	*Mean square*	*F-ratio*	*P-value*
MAIN EFFECTS					
A:Parameter	0	2	0	0,00	1,0000
B:Method	0,774991	1	0,774991	109,90	0,0000
INTERACTIONS					
AB	0,160132	2	0,080066	11,35	0,0000
RESIDUAL	0,592343	84	0,0070517		
TOTAL (CORRECTED)	1,52747	89			

Table 13: Analysis of variance for sludges



Graph 14: Graphs of interactions for sludges

The graph above (graph 14) confirms the previous observations. For Al and K deviations between methods are similar and more significant than Cr.

Comparison Sludges – Sediments

To compare results in sediment and sludges, Al and Cr were studied because there are the two common parameters for the two matrices. The common methods A and B have also been taken into account. To this end, relative means of methods A and B for sediments have been re-calculated without taking into account method C. Indeed, the “total” dissolution is not or barely used by laboratories for sludges whereas it is used for sediments.

Thus for example in table 14 below for 16M9.1 proficiency test, in the first part of this study, relative means with the 3 methods A, B and C were calculated. The method A had a relative mean of 0,78, the method B 0,52 and method C 1,70. Without taking into account the method C, the relative mean of method A is 1,20 and relative mean of method B is 0,79.

PT	Parameter	Unit	Mean by method (m)	Mean of all methods (M)	Relative mean m/M
Taking into account method C					
16M9.1	Al Method A	g/kg of dry matter	25,327	32,318	0,78
	Al Method B		16,783		0,52
	Al Method C		54,845		1,70
Without taking account method C					
16M9.1	Al Method A	g/kg of dry matter	25,327	21,055	1,20
	Al Method B		16,783		0,79

Table 14: Example of calculation of relative mean without method C

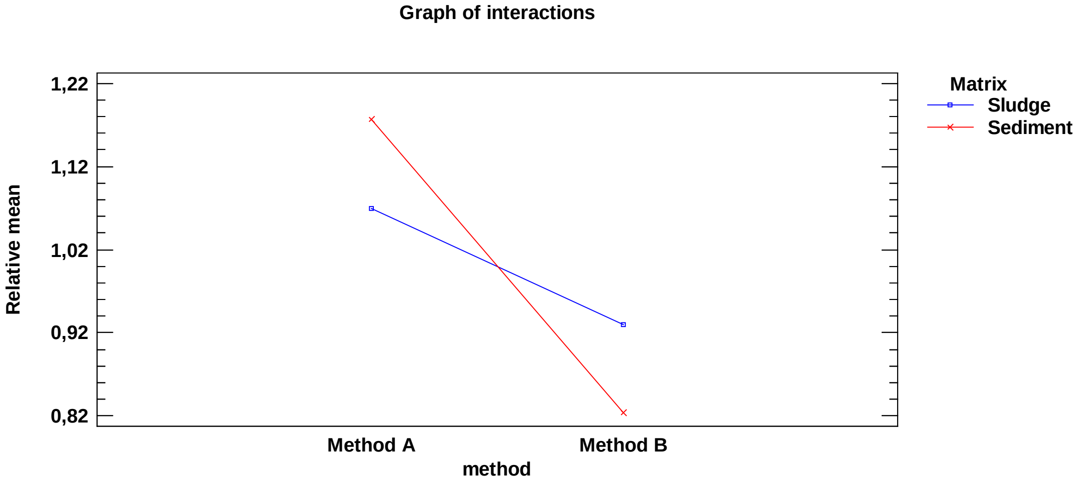
After analysing the relative means as a function of the parameter, the method and the matrix with an analysis of variance (table 15), we can see that they significantly vary depending on the method (probability inferior to 0,01). Furthermore, the effect is also variable from a parameter to another (probability of the interactions of factors parameters/methods inferior to 0,01) and from a matrix to another (probability of the interactions of factors matrices/methods inferior to 0,01).

Analysis of variance for relative mean

Source	*Sum of squares*	*Df*	*Mean square*	*F-ratio*	*P-value*
MAIN EFFECTS					
A:Parameter	0	1	0	0,00	1,0000
B:Method	1,74983	1	1,74983	255,93	0,0000
C: Matrix	0	1	0	0,00	1,0000
INTERACTIONS					
AB	0,312344	1	0,312344	45,68	0,0000
AC	0	1	0	0,00	1,0000
BC	0,329107	1	0,329107	48,14	0,0000
RESIDUAL	0,745236	109	0,00683703		
TOTAL (CORRECTED)	3,08659	115			

Table 15: Analysis of variance Sediments – Sludges

Deviations between methods are more significant for sediment than sludge. Furthermore, methods A and B follow the same trend in sludge and sediment: method A gives higher results than method B, in sludge or in sediment and for all parameters (graph 15).



Graph 15: Graph of interactions sediment - sludge

4. INTERPRETATION OF DEVIATIONS OBSERVED

In sediments or in sludges, the dissolution method that gives the lowest results is the “partial” dissolution method (method B). The *aqua regia* dissolution method in a closed system with microwave heating (method B) gives intermediate results between “partial” dissolution methods (method B) and “total” dissolution methods (method C).
“Partial” dissolution methods don’t enable to analyse the totality of the metals. However, microwave heating allows the sample to be instantly and completely irradiated hence a faster heating speed than the other heating methods. These temperature rises are more significant with the use of closed reactor which enable also a rise of the pressure during the mineralization.[1] Thus, for *aqua regia* dissolution methods, the microwave heating in a closed system enable to access to a bigger part of metal than the other heating methods less energetic.

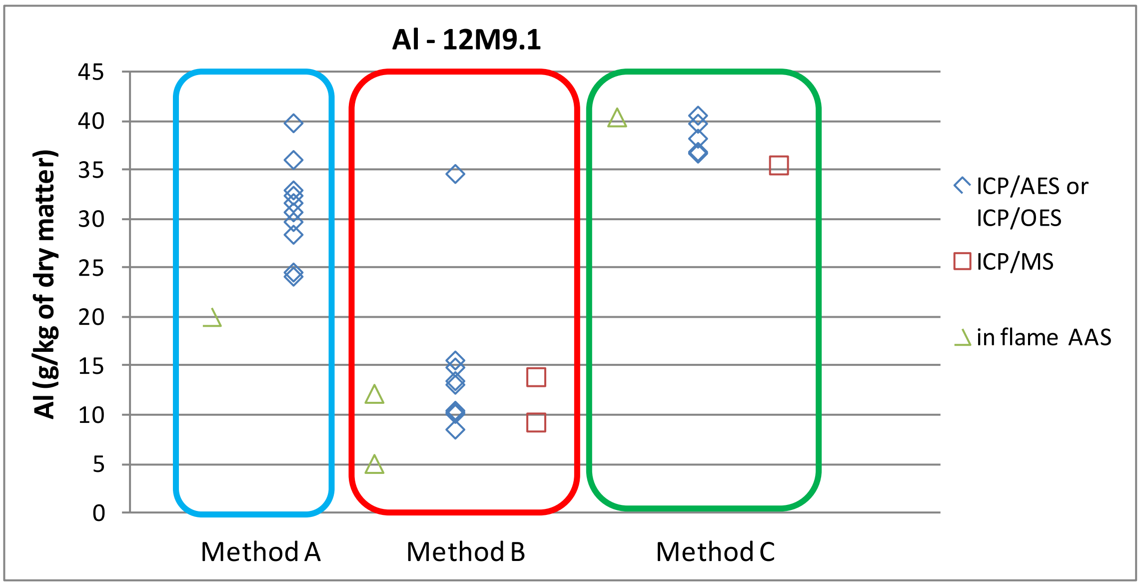
This part will concern several factors which can influence the deviations between dissolution methods observed: the analytical method, the concentration level of the metal in the matrix, the content in total organic carbon (TOC) and the type of sediment or sludge implemented.

4.1. INFLUENCE OF THE ANALYTIC METHOD

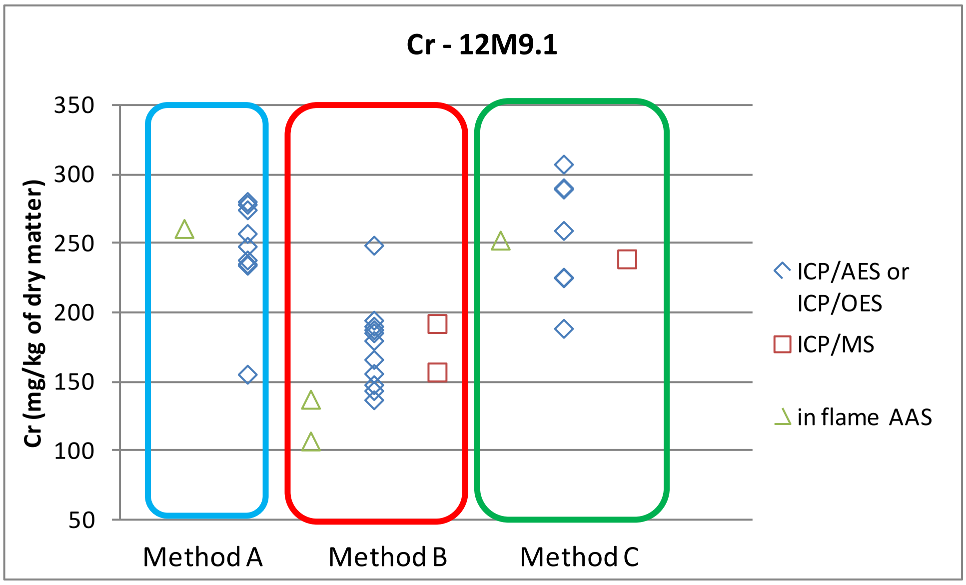
We checked that deviations between dissolution methods weren’t caused by the analytical technique used by the participants. For this, results of participants were examined regarding the dissolution methods and the analytical methods to check that analysis and dissolution methods aren’t correlated; if this was the case it would be impossible to tell if the deviations observed are caused by the dissolution method or the analytical method.
In most cases, the analytical methods used in sludges and sediments are optical-ICP, ICP-MS and in flame AAS.

Sediments – Programme 9

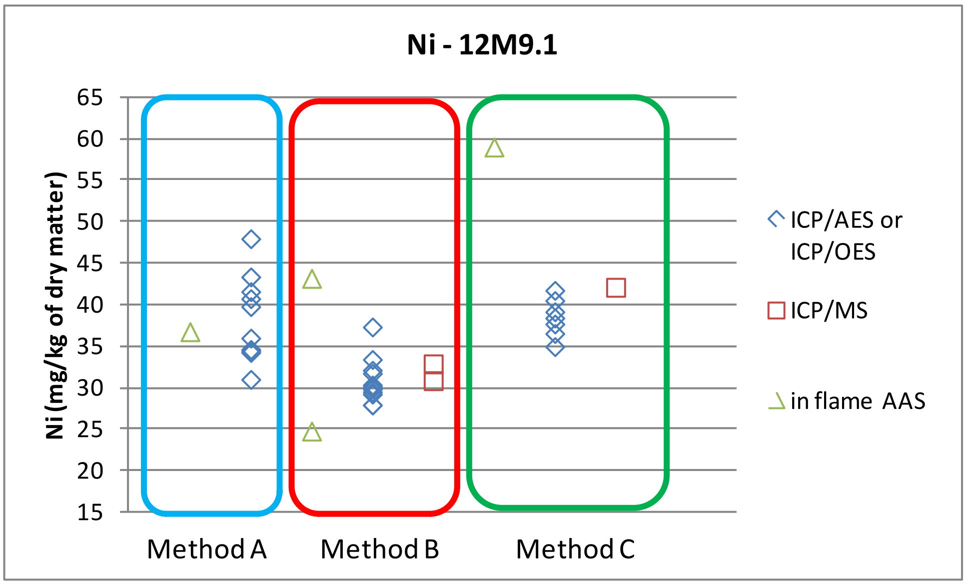
For sediments, a proficiency test representative of analytical techniques used (PT 12M9.1) has been studied. It is a proficiency test where a majority of dissolution methods and analytical methods are represented. Graphs below (graphs 16, 17 and 18) presents results of participants regarding the dissolution methods used for the three analytical techniques.



Graph 16: Influence of the analytical technique for Al in sediments



Graph 17: Influence of the analytical technique for Cr in sediments

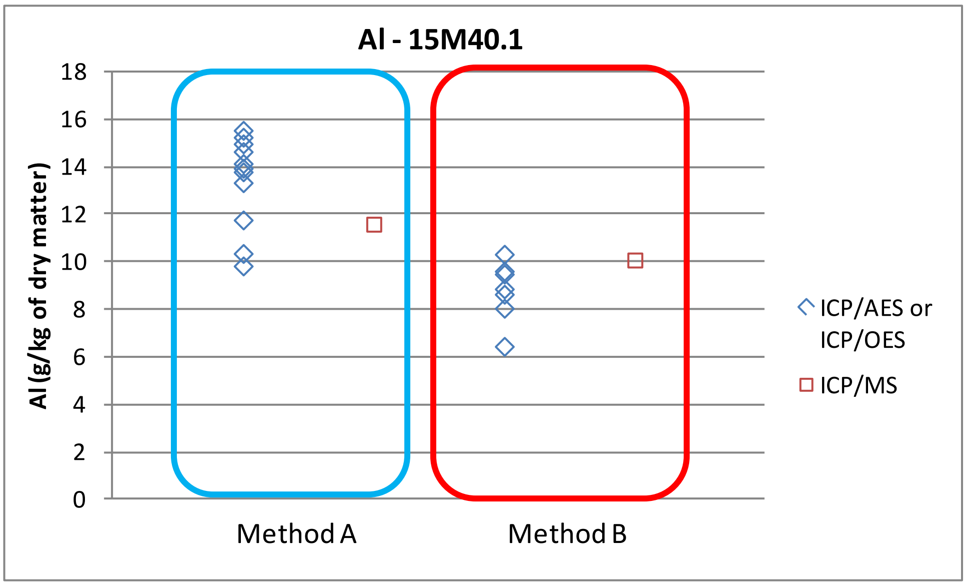


Graph 18: Influence of the analytical technique for Ni in sediments

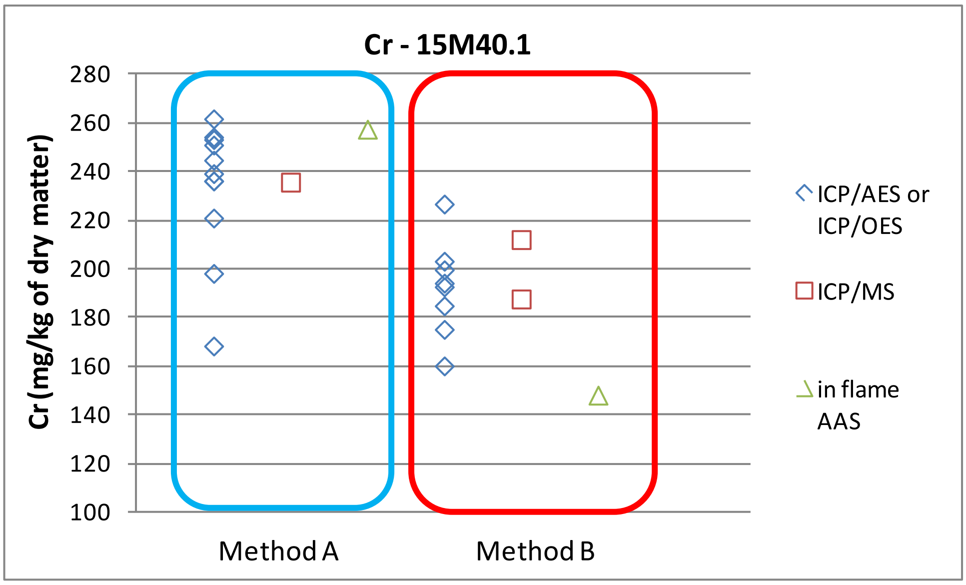
The majority of laboratories use ICP/OES or ICP/OES and they use indifferently the 3 dissolution methods. Thus there is no correlation between the analytical methods and the dissolution methods, deviations observed are not caused by the analytical method.

Sludges – Programme 40

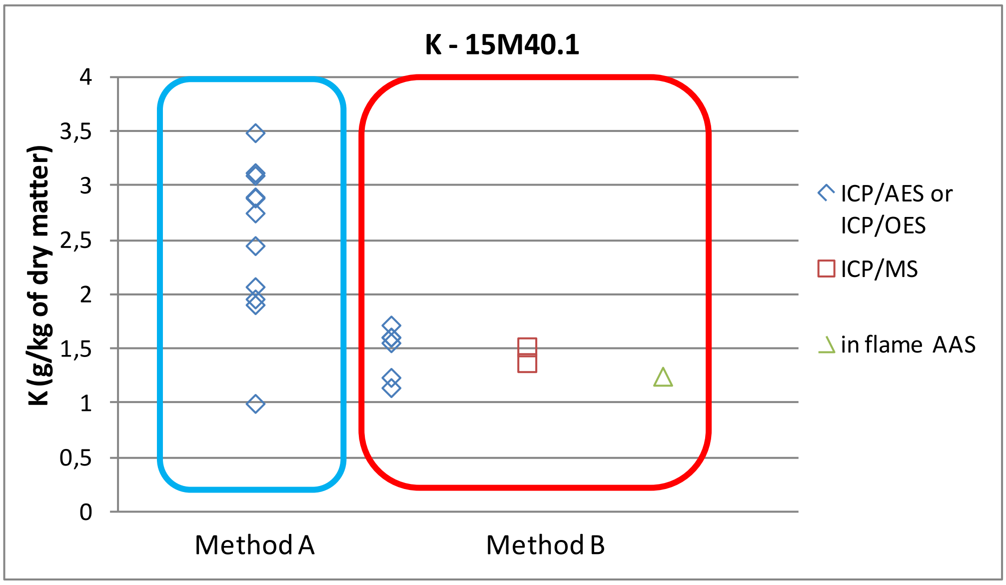
For sludges (programme 40), the proficiency test 15M40.1 has been studied. It is a test where a majority of dissolution methods and analytical methods are represented.



Graph 19: Influence of the analytical technique for Al in sludges



Graph 16: Influence of the analytical technique for Cr in sludges



Graph 21: Influence of the analytical technique for K in sludges

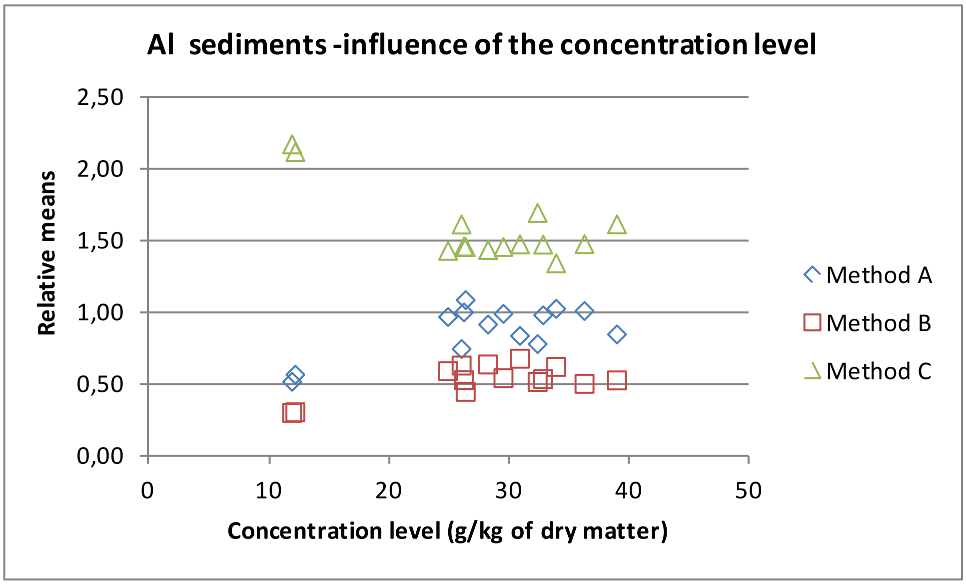
As for sediments, few laboratories use ICP/MS and in flame AAS (graphs 19, 20 and 21) and there is no correlation between analytical techniques and dissolution methods. Indeed, the main method, ICP/AES or ICP/OES is used with the two dissolution methods. In sludges, deviations observed aren't caused by the analytical techniques used.

4.2. INFLUENCE OF THE CONCENTRATION LEVEL

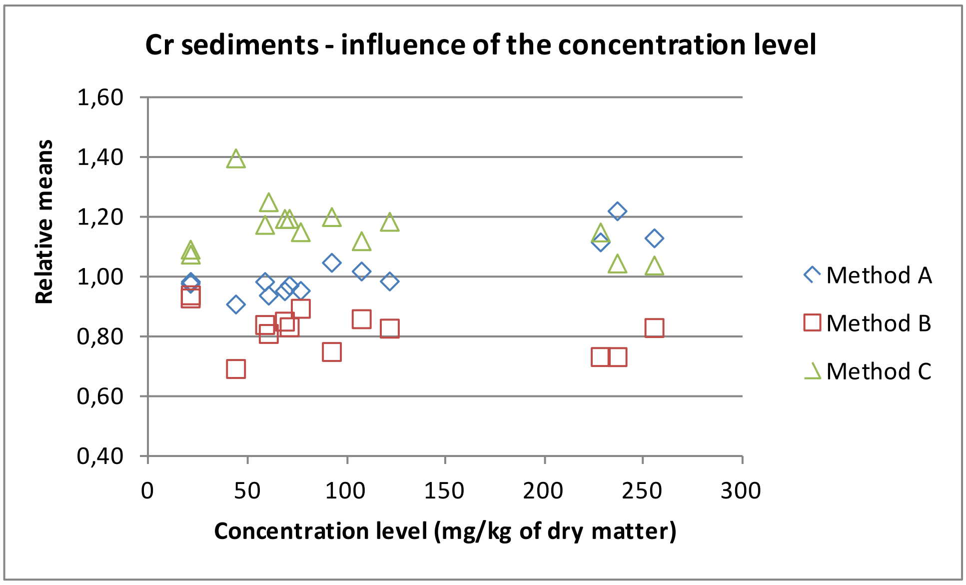
Deviations between means of methods are compared to the concentration level of metals in the matrix to see if the concentration level has an impact on the significance of deviations observed. Note that metals "naturally" exist in the matrix (no artificial spiking carried out during the tests preparation).

Sediments – Programme 9

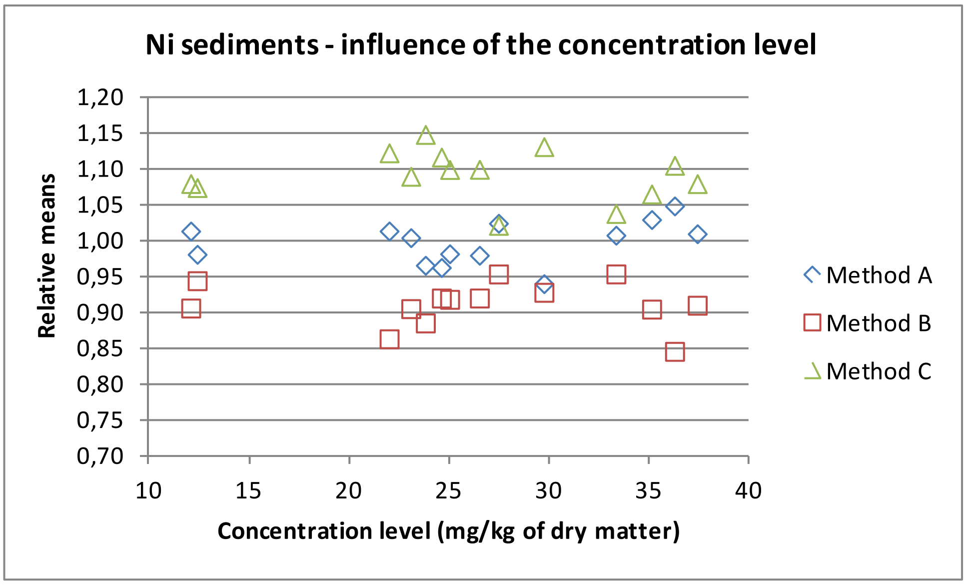
Graphs below (graphs 22, 23 and 24) present the deviations between dissolution methods as a function of the concentration level.



Graph 17: Influence of the concentration level for Al in sediments



Graph 18: Influence of the concentration level for Cr in sediments

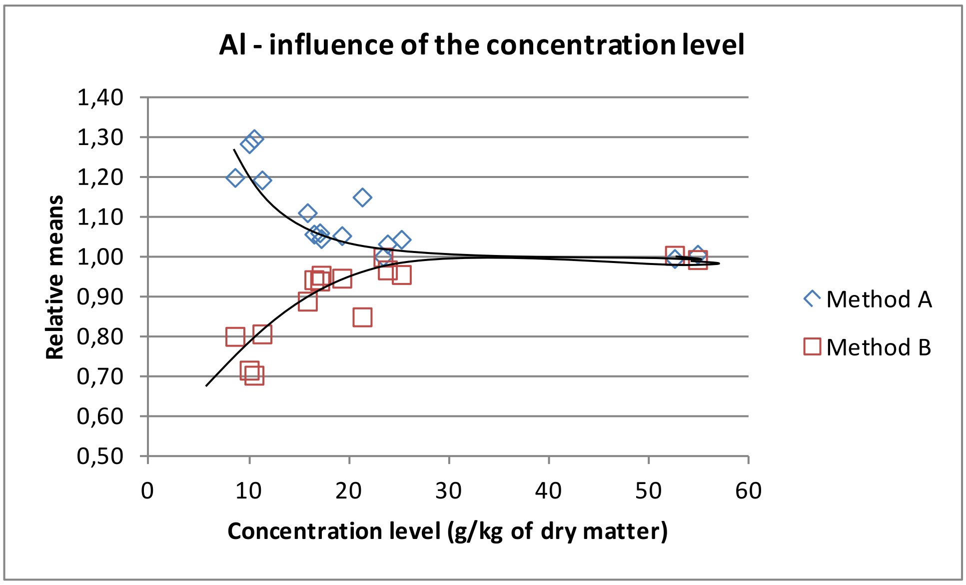


Graph 19: Influence of concentration level for Ni in sediments

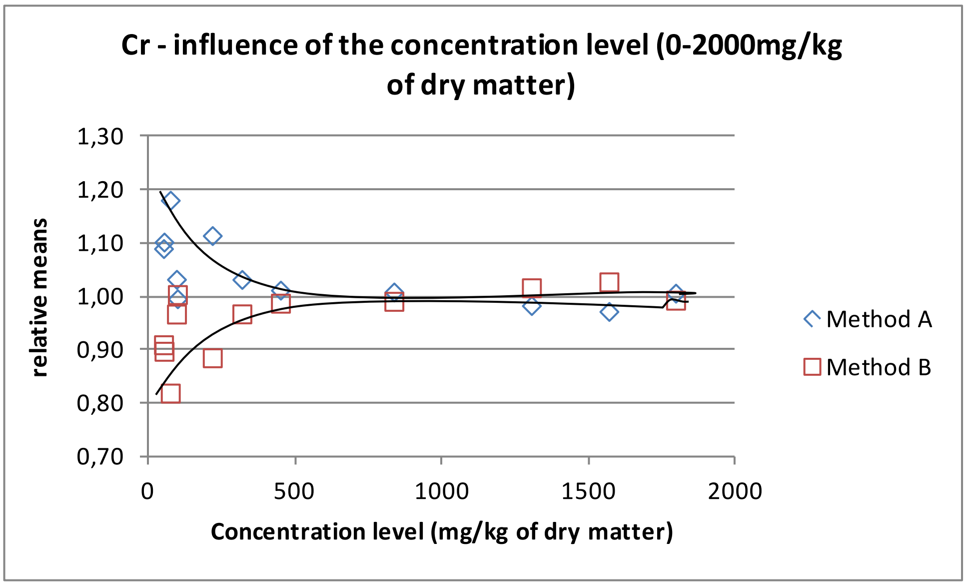
For Al, deviations are quasi constant for a concentration level superior to 20g/kg of dry matter. For two tests with a concentration level <20g/kg of dry matter, deviations are more significant.
For Cr and Ni, the concentration level doesn't seem to have an impact on the deviations between methods, on the concentration range studied.

Sludges – programme 40

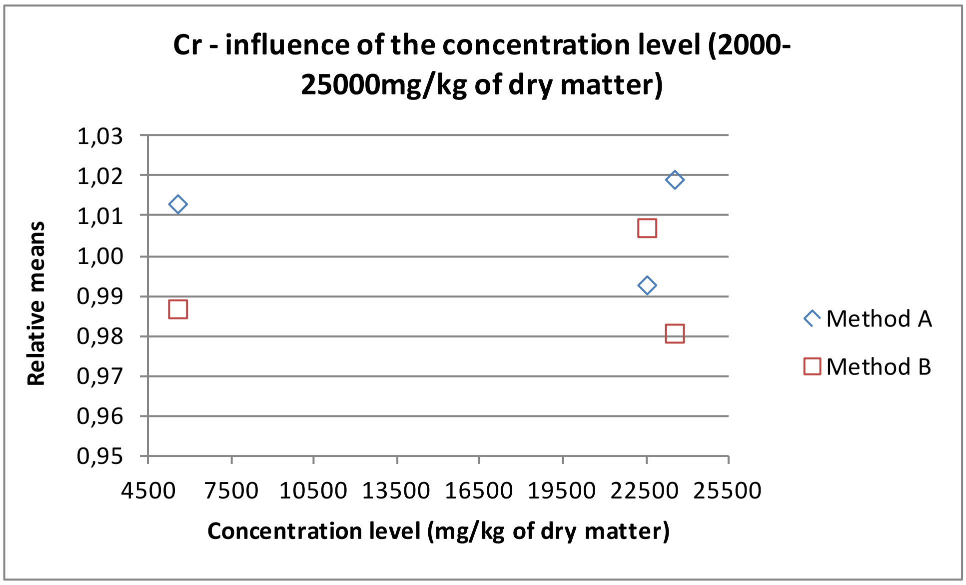
Graphs below (graphs 25, 26, 27 and 28) show the influence of the concentration level on the deviations obtained for sludges.



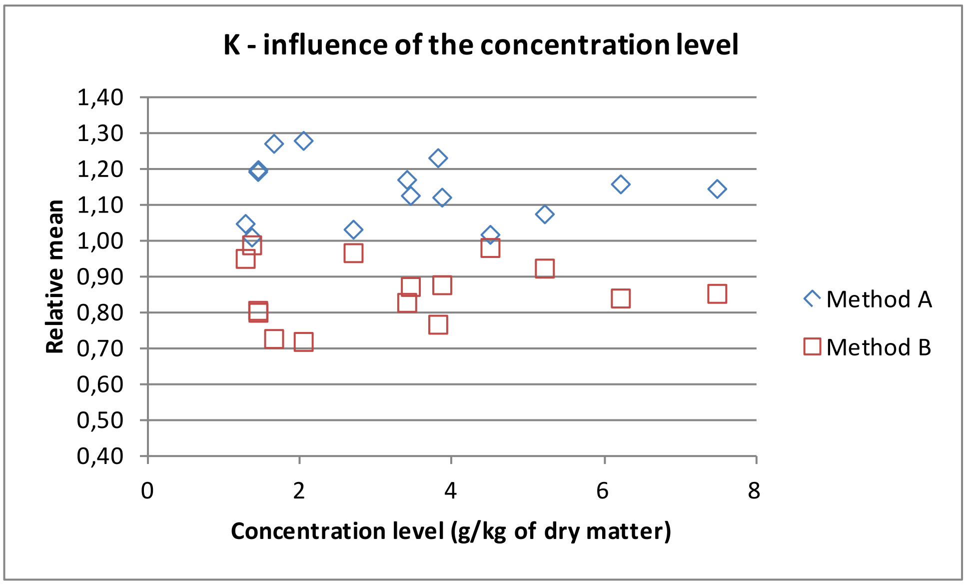
Graph 25: Influence of the concentration level for Al in sludges



Graph 26: Influence of the concentration level for Cr in sludges (0-2000mg/kg of dry matter)



Graph 27: Influence of the concentration level for Cr in sludges (2000-25000mg/kg of dry matter)



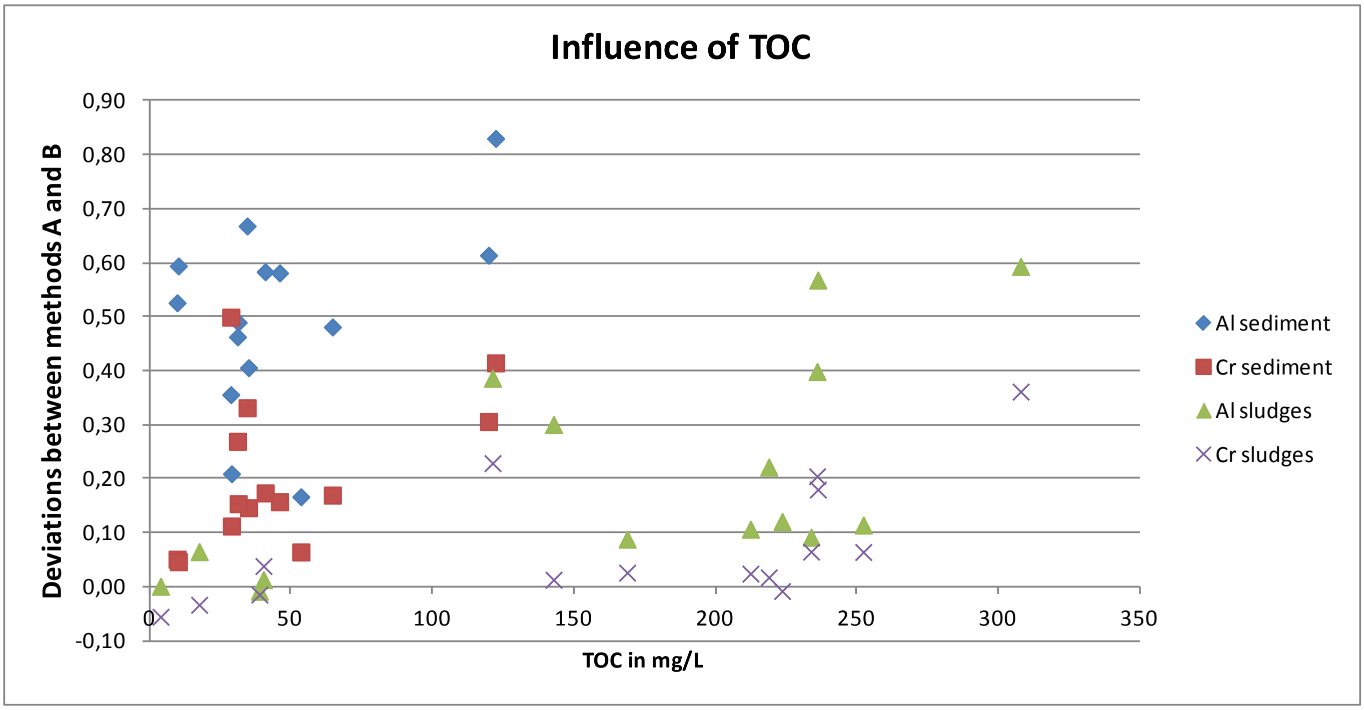
Graph 20: Influence of the concentration level for K in sludges

For Al, we can see a trend: deviations between methods are more significant for the lowest concentration levels. The deviations tend to 0 (relative means to 1) when the content is superior to around 30g/kg of dry matter.
For Cr, deviations between methods are also more significant for the lowest concentration levels. Deviations tend to 0 (relative means to 1) form around 800mg/kg of dry matter. For the highest concentration level (superior to 2000mg/kg of dry matter), deviations are also reduced.
For K, deviations between methods are quite constant on the concentration range. The concentration level doesn't seem to have an impact on the deviations.

As a conclusion, in sediments, the concentration level doesn't seem to have an impact on the deviation between methods, except for Al for concentrations <20g/kg of dry mater. However, for Al and Cr in sludges, deviations between methods are more significant for the lowest concentration levels: deviations tend to 0 from 30mg/kg of dry matter for Al and from 890mg/kg of dry matter for Cr.

4.3. INFLUENCE OF THE TOC

Deviations between means of methods are compared to the total organic carbon (TOC) in the matrix to see if TOC has an impact on the significance of deviations observed in sediments and sludges. In our tests, the TOC is a parameter analysed by the participants in the two matrices. Thus we used these data.
In order to compare the results in sediments and sludges, Al and Cr were studied because they are the two common parameters in the two matrices. The common methods A and B were also studied. The relative means were recalculated without the method C as indicated in the paragraph "data treatment – Comparison sludges – sediments".
The graph below (graph 29) presents the deviations between the relative means of methods A and B as a function of the content in TOC present in the matrix for each test.



Graph 29: Influence of TOC on deviations observed

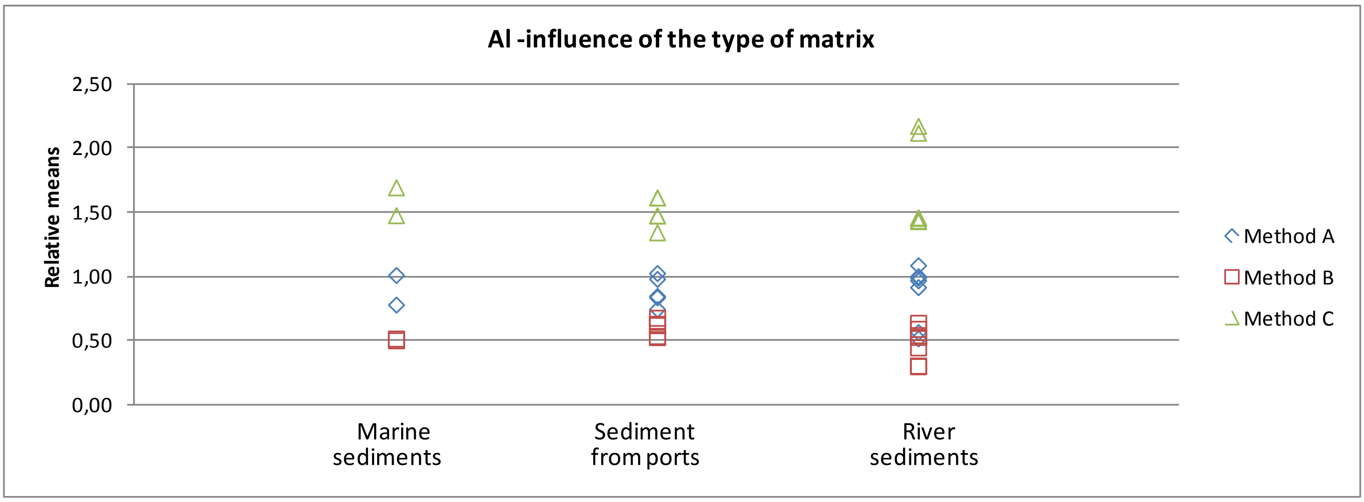
The content in TOC is higher for sludges than for sediments.
For sediments, the deviations aren't explained by the content in TOC (Spearman's rank correlation non significant).
For sludges, for contents in TOC inferior to 50mg/L, deviations are lower for Cr and Al. There is a correlation between the content in TOC and the deviations between methods A and B, particularly visible for Al (Spearman's rank correlation coefficient of 0,725).

4.4. INFLUENCE OF THE TYPE OF SEDIMENTS OR SLUDGES

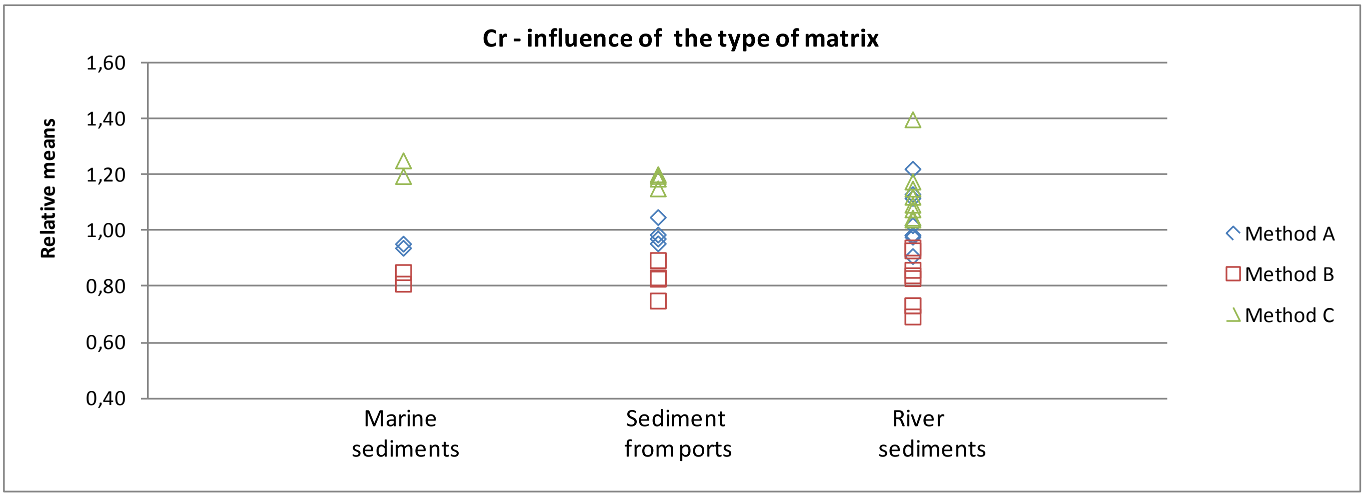
The type of sediments or sludges was also studied in order to see its influence on deviations observed.

Sediments – programme 9

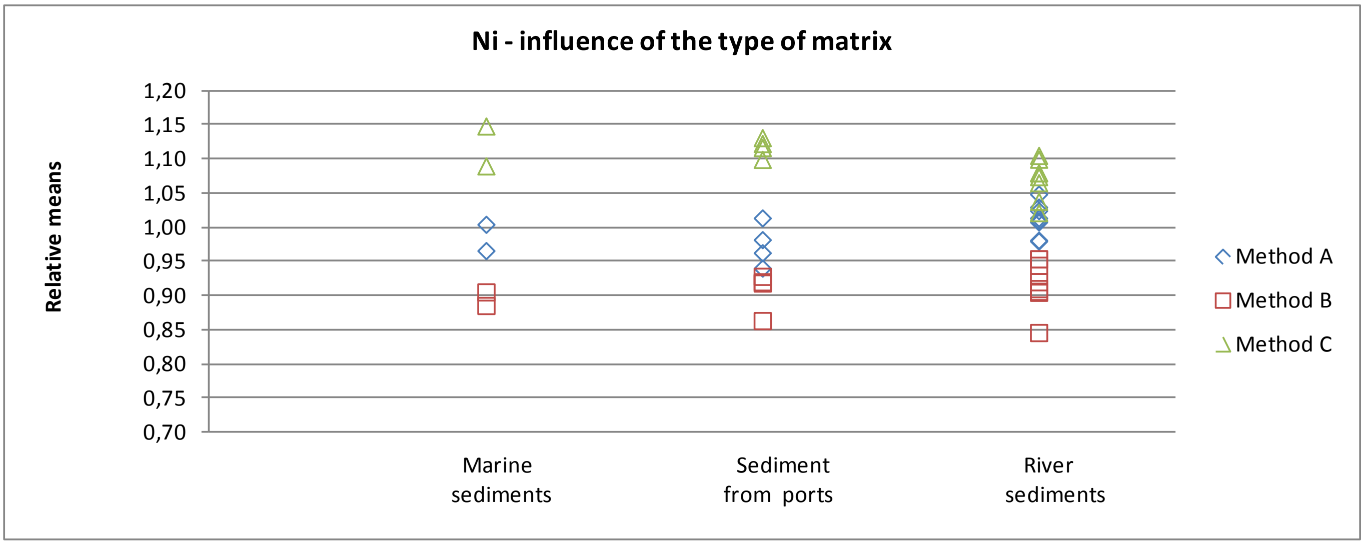
Different types of sediments were used during our proficiency tests: two marine sediments, five sediments from ports and seven river sediments. The graphs below represent, for each parameter studied, the relative deviations observed for each test as a function of the type of sediments implemented (graphs 30, 31 and 32).



Graph 21: influence of the type of sediments on the deviations between methods for Al



Graph 22: influence of the type of sediments on the deviations between methods for Cr

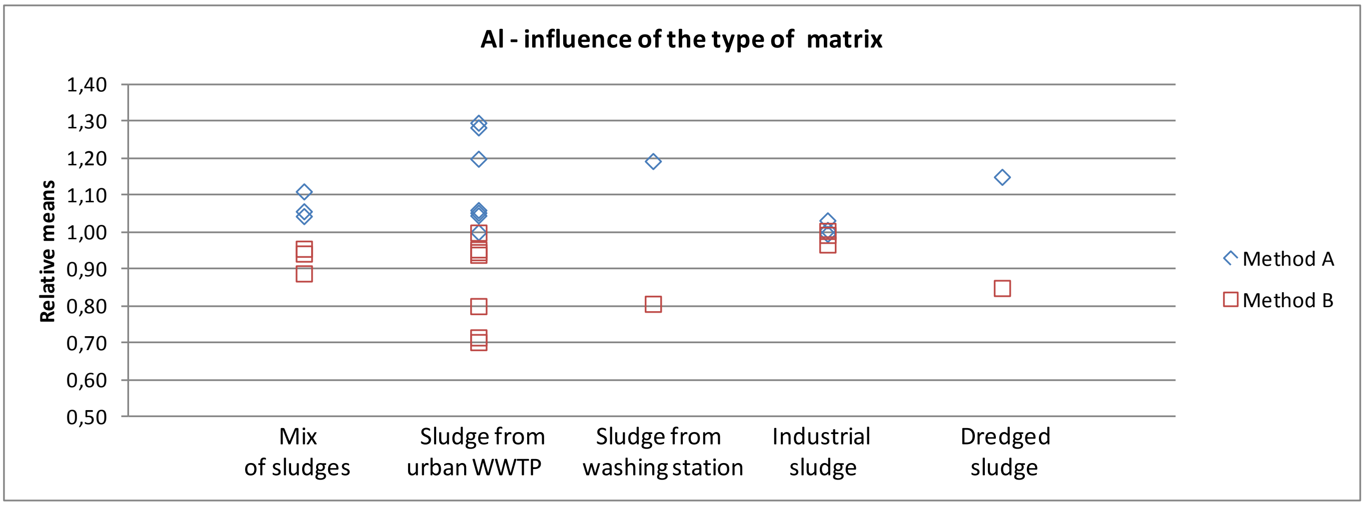


Graph 23: influence of the type of sediments on the deviations between methods for Ni

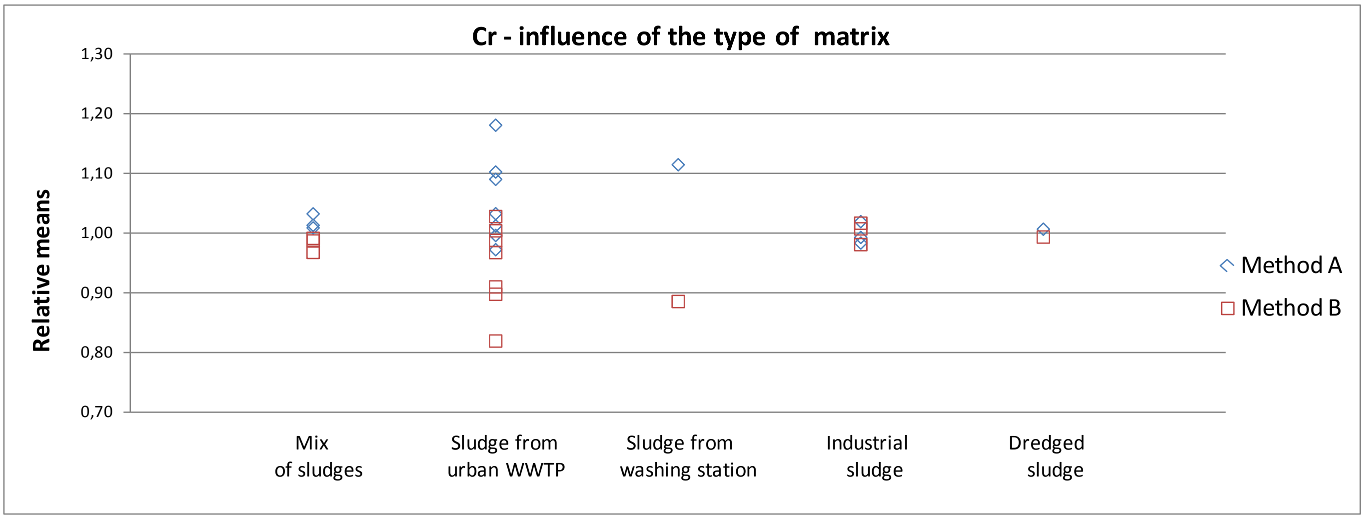
For the 3 metals, deviations are similar for each sediment implemented. Note however, for Al that deviations are higher for river sediments.

Sludges – programme 40

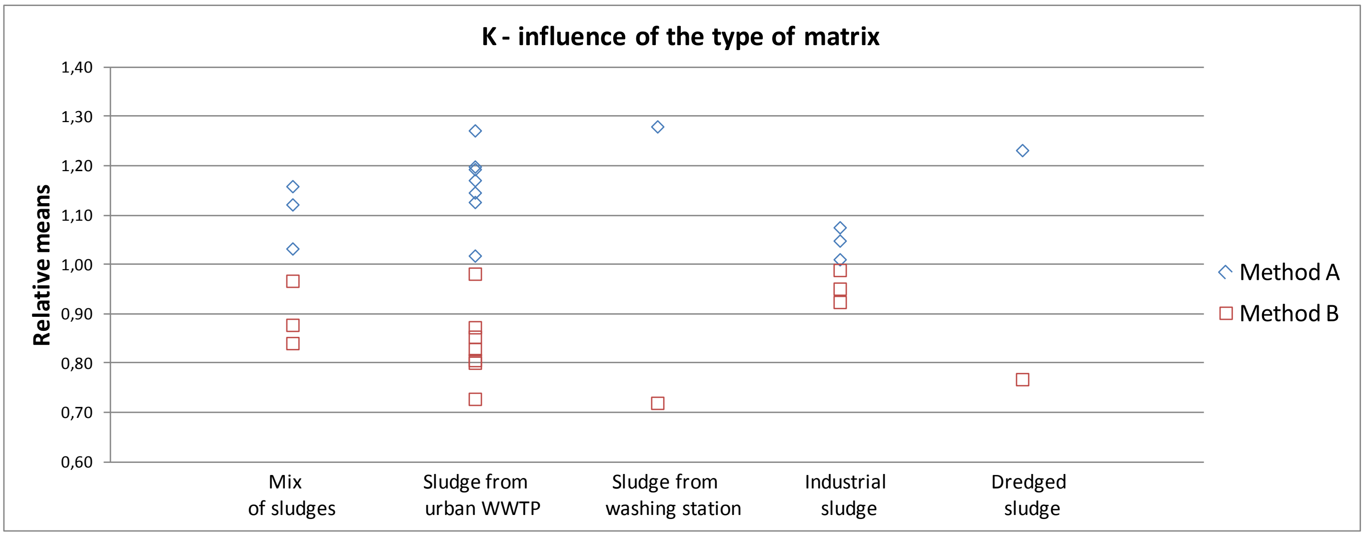
The different types of sludges used during our proficiency tests are a dredged sludge, three industrial sludges, seven sludges from urban waste water treatment plant (urban WWTP) and one sludge from washing station. Three mixes of sludges are also used. Graphs below represent for each parameter studied, the relative deviations between methods A and B observed during each test as a function of the type of sludge used (graphs 33, 34 and 35).



Graph 24: Influence of the type of sludge on the deviations between methods for Al



Graph 25: Influence of the type of sludge on the deviations between methods for Cr



Graph 26: Influence of the type of sludge on the deviations between methods for K

For the 3 parameters, the deviations tend to be less important in industrial sludges than in the other type of sludges.

The type of sediment or sludge used doesn't seem to explain in a definitive way the deviations between dissolution methods. However, it doesn't exclude that the intrinsic composition of the matrix can have an influence on the deviations observed. Indeed, for example, the ISO 14869-3 standard which presents a dissolution method with hydrofluoric acid, hydrochloric acid and nitric acid with a pressurised microwave heating indicates enabling the total dissolution of metals but that some refractory compounds such as SiO2, TiO2, spinel, AlO_3, or other compounds could remain as residual form. It is thus recommended to use alkali fusion. That is a good example of the fact that all methods don't have the same efficiency in all type of matrix. Furthermore, some studies [2], [3] ,[4], [5}, [6] show that deviations observed between "total" methods and *aqua regia* extraction are caused by the presence of silicates, or aluminium, iron or manganese oxides which aren't totally dissolved by the *aqua regia* and on which some metals can bind.

Sediments and sludges are complex matrices where several phenomena can influence the behavior of metal pollutants in these matrices like hydrodynamic and transfer processes and physicochemical and biological mechanisms.

The main factors that influence the metal mobility in soils are the pH, the redox potential, the temperature and the humidity of the soil: the speciation of the metal changes with the pH and influences the fixation on the solid phase. The aeration degree of the soil modifies the mobility of metals for which reduced forms are more mobile in soil in oxidized form. The temperature and the humidity play also indirect part encouraging the biological activity of the soil and so the production of acid or complexing substances[7].

Thus, regarding the intrinsic composition of the matrix and the environment factors, metals are bound in different ways to the matrix making their dissolution more or less easy. For two matrices of identical type, for example two river sediments from different origins, the dissolution of metals won't be identical and deviations between methods can be seen. Furthermore, the presence of several metals in the matrix at different concentration levels could possibly interfere with the analysis.

5. CONLUSION

Deviations between dissolution methods have often been highlighted during our proficiency tests in sludges and sediments. However, in soils, very few deviations between methods were observed.

In sediments, deviations the most frequently observed during our test concern Al, Cr and Ni. For sludges deviations appear frequently for Al and K. This study was carried out on these parameters. For sludges, Cr was also studied to be able to compare the two matrices even if the frequency of deviations for this parameter is lower.

The table 16 below summarizes the mean deviations between dissolution methods observed and indicates for which methods the highest results are found.

	Mean deviations observed between relative means		
Sediments			
Parameter	Methods A and B	Methods A and C	Methods B and C
Al	35%	71%	106%
Cr	19%	15%	34%
Ni	8,5%	9,3%	18%
Direction of deviations observed	Method C > Method A > Method B		
Sludge			
Al	20%	No method C studied in sludges	
Cr	7,4%		
K	28%		
Direction of deviations observed	Method A > Method B		

Table 16: Summary of deviations between dissolution method in sediments and sludges

Method A: HCl/HNO_3 in a closed system with microwave heating; Method B: HCl/HNO_3 under reflux or in a heating block (programme 9) or Boiling HCl/HNO_3 in a glass tube; Method C: hydrofluoric/perchloric etching, alkali fusion / alkaline fluxes, alkali fusion / oxidizing fluxes

In sediments and sludges, significant deviations are observed between all dissolution methods studied:

- In sediments, “total” dissolution methods (hydrofluoric/perchloric etching, alkali fusion…) give higher results than “partial” dissolution methods (dissolution methods with *aqua regia*) and the *aqua regia* dissolution method in a closed system with microwave heating. This method gives intermediate results between the “total” dissolution method and the “partial” dissolution method. On average, deviations are more significant for Al than for Cr and Ni. They also vary more from a test to another for Al than for Cr and Ni.
- In sludges, “partial” dissolution methods (*aqua regia* dissolution methods) give lower results than the *aqua regia* dissolution method in a closed system with microwave heating. K has the most significant deviations between methods, then Al and Cr. However, the variation of deviations between dissolution methods from a test from another is quite similar for the three parameters.

We checked that deviations observed weren’t caused by potential deviations between analytical techniques. Indeed, in sediments or sludges, the three analytical techniques generally used (ICP/MS, in flame AAS and ICP/AES or ICP/OES which is the most used) are carried out indifferently with the dissolution method. This lack of correlation between dissolution method and analytical method enables to say that the deviations observed aren’t caused by potentials deviations between analytical techniques.

In sediments, the concentration level doesn’t seem to have an influence on the deviation, except for Al for concentrations <20g/kg of dry matter for which deviations between dissolution methods re more significant.
However, for Al and Cr in sludges, it clearly appears that the concentration level has an influence on deviations observed. Indeed, the lower the concentration level is, the higher are the deviations between dissolution methods.

In sediment, the content in TOC (total organic carbon) doesn’t influence the deviations observed. But in sludges, there is a correlation between the content of TOC in the matrix and the deviations between methods.

Lastly, deviations between methods are similar for each sediment used, except maybe for Al. In sludge, deviations observed for industrial sludges seem more reduced than the other types of sludges. Deviations observed are more important for sediment compared to sludge.
Deviations between dissolution methods vary according to the intrinsic composition of the matrix: some refractory compounds like SiO2, TiO2, spinel of AlO_3 or other compounds can remain as residual form after dissolution. Furthermore, some studies have shown that deviations between “total” dissolution methods and *aqua regia* extraction are caused by the presence of silicate or aluminium, iron or manganese oxides which are not completely dissolved by the *aqua regia* and on which some metals can bind. Thus the intrinsic composition of the matrix can influence the dissolution of the metals

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Normative references

NF ISO 11466: Soil quality - Extraction of trace elements soluble in *aqua regia*
NF EN 13346: Characterization of sludges. Determination of trace elements and phosphorous. *Aqua regia* extraction methods
NF EN 16174: Sludge, treated biowaste and soil - Digestion of *aqua regia* soluble fractions of elements
NF ISO 12914: Soil quality - Microwave-assisted extraction of the *aqua regia* soluble fraction for the determination of elements
NF X31-147: Quality of soils - Soils, sediments – Total dissolution method by acid attack
NF ISO 14869-1: Soil quality - Dissolution for the determination of total element content - Part 1: Dissolution with hydrofluoric and perchloric acids
NF ISO 14869-2: Soil quality - Dissolution for the determination of total element content - Part 2: Dissolution by alkaline fusion
NF ISO 14869-3: Soil quality - Dissolution for the determination of total element content - Part 3: Dissolution with hydrofluoric, hydrochloric and nitric acids using pressurised microwave technique