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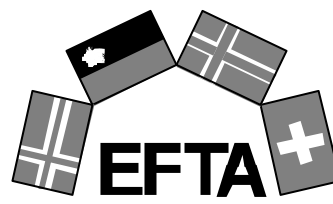
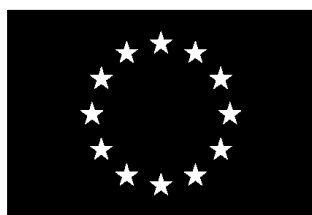
**CENTC 264/WG 14 “Reference Method for the  
Determination of Lead, Cadmium, Arsenic and Nickel in  
Ambient Air”**

## **Statistical Evaluation of Field Test Data (Minimum Validation Programme)**

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**June 2002**

**Contract BC/CEN/97/49.1**



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## 1 Introduction

This report summarises the results of the statistical evaluation of the Field Validation Programme of CEN/TC WG 14. This programme aims at the characterization of the reference method that is going to be described in the CEN Standard "Air Quality – Reference method for the measurement of Pb/Cd/As/Ni in ambient air for the implementation of EC Air Quality Directives".

The requirements of the 1st Daughter Directive [1] and the Position Paper on Cadmium, Arsenic and Nickel [2] in the form of maximum allowable uncertainties are the basis for the characterization of the methods applied.

The determination of the Expanded Uncertainty has been performed in line with the GUM [3] and the "Terms of Reference" [4] that have been laid down by the CEN TC 264. For the evaluation of the uncertainty of the reference method WG14 has developed a statistical model to cover all uncertainty contributions as required by the GUM. In the same way the Guide of CEN TC 264 "Approach to Uncertainty Estimation" [5] was an important basis for the creation of that model.

Moreover performance characteristics as Repeatability and Reproducibility have been determined.

On the basis of laboratory and preliminary field tests an analytical method was agreed by the working group members and laid down in the analytical guidance document N 245. As variations of the analytical method both Graphite Furnace AAS and ICP-MS were taken into account. For the sampling process two types of filter material were applied, Quartz Fibre and Membrane (Cellulose acetate) filters.

At four sampling sites in Europe 80 days of sampling with 8 parallel samplers were undertaken, so that at the end of the Field Validation Test 640 sampled filters were available for the analytical determination.

The sampling sites were:

- Madrid (urban site)
- Avonmouth (industrial site near Bristol)
- Berlin (urban site)
- Hoboken (industrial site near Antwerp)

Four different sampling sites with distinct site characteristics were chosen in order to get as much information as possible on the performance of the reference method in different ambient conditions.

The field trials were carried out during the different seasons of a year to get information across different meteorological conditions.

Due to the fact that the uncertainty is dependent on the concentration of the elements in the ambient air, the four sampling sites represent four different data sets that can be used for the determination of the uncertainty at the limit value by extrapolation or interpolation.

The following laboratories participated in the Field Validation Programme:

- Lab A : Centro Nacional de Sanidad Ambiental,  
Instituto de Salud Carlos III (ISCIII), Spain
- Lab B : UK Consortium (Casella Stanger / CRE Group Ltd. / Harwell  
Scientifics Ltd.), UK
- Lab C : Vlaamse Milieumaatschappij (VMM), Belgium
- Lab D : Umweltbundesamt (UBA-DE), Germany /  
Umweltbundesamt (UBA-A), Austria

This report lays down the statistical basis of the evaluations, summarises the performance criteria "uncertainty", "repeatability" and "reproducibility" and provides respective interpretations.

Moreover the several data sets were compared from different points of view to allow a better characterization of the methods in addition to the statistical evaluation of the performance characteristics.

## 2 Summary: Results of the statistical evaluation

This section shows in compact, tabulated form the results of the statistical evaluation. The results can be divided into two parts. The first part shows the results of the **Uncertainty calculation**, the second part the determination of **Repeatability** and **Reproducibility**, as well as the comparison of the analytical techniques (GF-AAS / ICP-MS) and filter materials (Quartz-fibre filter / Membrane filter).

In this section neither explanation of the statistical model nor interpretation is given. These topics are handled later in the following sections.

The results of Table 1 are calculated according to the statistical model of WG 14 as described in section 3.2.2 "Evaluation of the Uncertainty".

**Table 1: Summary of the Expanded Uncertainties at the limit value in %**

	<b>AAS</b>	<b>ICP-MS</b>	<b>Requested</b>
Lead	7	12	25
Cadmium	13	17	25
Arsenic	18	14	40
Nickel	21	9	40

The results in Table 1 point out that both techniques of the Reference Method of WG14 meet the requirements!

The results of Tables 2 and 3 are calculated as described in section 4 "Statistical evaluation of the data sets".

**Table 2: Repeatability and Reproducibility**

Lead	Mean conc ng/m <sup>3</sup>	AAS - Technique		ICP-MS-Technique	
		Mean Repeatability* (%)	Reproducibility (%)	Mean Repeatability* (%)	Reproducibility (%)
Madrid	25	8	9	16	18
Bristol	85	5	8	9	10
Berlin	26	7	10	9	11
Antwerp	944	4	4	5	9
<b>Cadmium</b>					
Madrid	0,35	25	34	45	41
Bristol	3,78	8	10	21	24
Berlin	0,36	10	19	17	16
Antwerp	9,30	5	7	7	14
<b>Arsenic</b>					
Madrid	0,7	18	37	23	28
Bristol	1,7	15	22	10	12
Berlin	3,3	7	16	11	12
Antwerp	82,8	6	13	5	7
<b>Nickel</b>					
Madrid	1,5	93	94	88	89
Bristol	4,0	36	41	35	46
Berlin	3,6	22	40	25	37
Antwerp	15,8	15	21	8	9

\* Repeatability averaged across all laboratories

**Table 3: Mean Repeatability and Reproducibility (%) across all sites**

Element	AAS		ICP-MS	
	Repeatab.	Reproducib.	Repeatab.	Reproducib.
Lead	6	8	10	12
Cadmium	12	17	22	24
Arsenic	11	22	13	15
Nickel	41	49	39	46

### 3 Uncertainty

As already mentioned above the 1<sup>st</sup> Daughter Directive (incl. Lead) as well as the Position Paper on Cadmium, Arsenic and Nickel demands maximum uncertainties of the methods applied for the measurements in ambient air.

Therefore WG 14 has developed a statistical model to cover all uncertainty contributions. In this section the development of the model, the description of the statistical approach and the results are laid down in detail.

#### 3.1 History of the development of the statistical approach

When WG 14 started its work in 1996 there was no requirement to evaluate the “Measurement Uncertainty”. At that time the main criteria were the Repeatability and the Reproducibility of the measurement method, which had to be evaluated by comparison tests in the field. To fulfil these requirements the WG decided at an early stage (first WG 14 meeting in 1996) to specify a Minimum Validation Programme (MVP) that should comprise both laboratory and field validation work in order to determine the performance characteristics of the method.

The intention of the WG was to carry out laboratory tests to build a common basis for the analytical method that should be applied later in the Field Validation Programme (FVP).

Following laboratory tests a second and third part of the MVP was performed, the Preparation of Field Test and the Preliminary Field Test. The reason was to transfer the experiences gained in the first steps of the validation work to the FVP.

The WG expected an improvement in analytical quality during the first three steps so that an optimised method could be applied in the Field Validation Programme.

About three years after WG 14 started work a growing discussion about the topic “Uncertainty in Measurement” came up within the TC 264 “Air Quality”. Soon it was clear that the calculation of the “Uncertainty” had to be based on the GUM. The problem remains of how to carry out such a calculation. Below this “how to” is referred to as “statistical approach”.

The development of the statistical approach of WG14 was started in January 2000, when WG 14 participated in the ad-hoc WG “Uncertainty” of CEN/TC 264. All working groups of CEN/TC 264 agreed to a common basis of the statistical approach as far as possible.

The first draft of the statistical approach of WG 14 was shown in the resulting document of the ad-hoc WG Uncertainty [5] as an example. In the meantime the statistical approach has been improved on several times and it was finally revised by a sub-working group of WG 14 at the beginning of 2002. The statistical approach that was finally proposed by this sub WG was agreed by the whole WG 14 in March 2002. It is laid down in WG 14 Document N270 and is the basis for all uncertainty calculations described in this report.

### 3.2 Introduction to the statistical approach

The following section describes the methods that have been applied to calculate the uncertainty of the Reference Method.

#### 3.2.1 Methods for data correction

Before the statistical evaluation can be performed the data sets had to be corrected for blanks and for outliers.

##### 3.2.1.1 Blank correction

For a better understanding of the term “Blank” a description of the several blank-types is given here:

- Reagent blank: This blank comprises only the reagents that are used without filter. For the determination a digestion with  $\text{HNO}_3/\text{H}_2\text{O}_2$  is performed.
- Lab filter blank: In addition to the reagent blank this blank covers concentration caused by the filter material.
- Field filter blank: This blank is the content that is found in a filter that was treated in the same way as a real sample, but without sampling. This value is used only for information as to whether a contamination problem has occurred, but it is not used for blank correction.

As agreed by WG 14, a lab blank correction has to be performed when the lab filter blank is above the limit of detection. This is the case when it is three times higher than the reagent blank standard deviation.

The reagent blanks were determined during the Preparation of Field Tests (Document N 168).

The following equations (1) and (2) show the calculation of the Detection Limit:

$$s_B = \sqrt{\frac{\sum_{i=1}^n (\bar{x} - x_i)^2}{n-1}} \quad (1) \quad \text{and} \quad LoD = t_{f=13, P=99} * s_B = 3 * s_B \quad (2)$$

Where:

- $s_B$  = Standard Deviation of the Reagent Blanks
- $n$  = Number of Reagent Blanks
- $x_i$  = Reagent Blank concentration
- $LoD$  = Limit of Detection

The Student's factor  $t$  for  $n = 14$  (degrees of freedom = 13) is 3.0.

The detection limits for AAS were always higher than the detection limits of ICP-MS. This is the reason for the fact that the AAS results are not very often corrected in comparison with the ICP-MS results. For calculation of the detection limit a probability of 99 % was chosen and only the results with a conjugated blank that was higher than the detection limit were corrected.

In Table 4 the detection limits of the various laboratories are listed as they were calculated according to the statistical procedure mentioned before.

**Table 4: Limits of Detection (based on reagent blanks)**

Laboratory (Technique)	Limit of Detection in ng/m <sup>3</sup>			
	Lead	Cadmium	Arsenic	Nickel
Lab A (AAS)	0.68	0.02	0.36*	0.52
Lab B (AAS)	0.93	0.09	0.39	0.69
Lab C (AAS)	0.48*	0.02	0.13	0.46
Lab D (AAS)	0.60	0.03	0.22	0.43
Lab B (ICP-MS)	0.08	0.000	0.36	0.24
Lab D (ICP-MS)	0.01	0.0001	0.09	0.01

\* Detection limit calculated from Reagent-Blanks of the field validation tests

The two marked limits of detection of laboratory A (Arsenic) and laboratory C (Lead) were taken over from the Field Validation Tests instead of from the Preparation of Field Tests, because the numbers decreased significantly during execution of the Field Tests.

A complete set of tables with the calculated blank–corrections is included in the annex.

### 3.2.1.2 Outlier correction

After having done the blank correction outliers were eliminated. There are many different outlier tests that could be applied. WG 14 agreed to use the Grubbs Test because this test is accepted in many international standards and guidelines.

The Grubbs Test is based on the following equation:

$$g = \frac{|x_i - \bar{x}|}{s} \quad (3)$$

where

- $x_i$  value with the largest deviation to the mean
- $\bar{x}$  mean value (calculated across all samplers on one day)
- $s$  standard deviation of the single results  $x$  across all samplers on one day
- $g$  test value for the Grubbs Test



When the value  $g$  is higher than the Grubbs test value  $g_{(n,99)}$  then an outlier is detected and excluded from the data set. Only a single application of the Grubbs test to a dataset is allowed. In this way only the significant outliers are eliminated.

A table with the number of eliminated outliers is attached in the annex of this report.

### 3.2.2 Evaluation of the uncertainty

After blank and outlier correction a valid data set for the uncertainty calculation is available.

As mentioned before WG 14 has developed a statistical model for the evaluation of the Expanded Uncertainty, which is laid down in document WG 14/N 270. The model is explained in detail in the following sections.

#### 3.2.2.1 Uncertainty Model

The statistical approach of WG 14 for the determination of the Expanded Uncertainty is based on the GUM taking the requirements of the Terms of Reference of CEN/TC 264 into account.

The analytical results that are necessary for the statistical calculations have been obtained from the Minimum Validation Programme as described above.

According to the GUM both random and non-random uncertainties have to be considered to estimate the **Combined Uncertainty** of the draft method.

$$u_c = \sqrt{u_r^2 + u_{nr}^2} \quad (4)$$

where

$u_c$	combined uncertainty
$u_r$	random uncertainty
$u_{nr}$	non-random uncertainty

The following table gives a list of all considered uncertainty contributions and also indicates whether they are random or not and whether they are obtained from the field tests or from other sources.

**Table 5: Uncertainty contributions**

Contribution	$U_r$	Covered by	$u_{nr}$	Covered by
Sampling volume	<b>Yes</b>	Field tests	Yes	$u_{vol} = \frac{5\%}{\sqrt{3}}$
Collection efficiency	<b>No</b>	-	Yes	Neglected because 99.5 % required by the reference method
Flow rate*	<b>Yes</b>	Field tests	No	
Transport	<b>Yes</b>	Field tests	(Yes)	Made insignificant by the reference method
Storage	<b>Yes</b>	Field tests	(Yes)	Made insignificant by the reference method
Analysis (digestion, calibration, measurement)	<b>Yes</b>	Field tests	Yes	CRM – measurement and uncertainty of the certificate of the CRM
Limit of detection	<b>Yes</b>	Field tests	No	-
Blank correction	<b>Yes</b>	Field tests	No	-

\* potentially changing  $PM_{10}$  characteristics by local climate conditions included

### 3.2.2.2 Random Uncertainty

The value  $u$  has been obtained from the field tests of WG 14 by calculating the standard deviation of the parallel measurements that completely covers the random uncertainty contribution. The field tests were carried out at four sampling sites in Europe using 8 sampling devices for parallel sampling. During this programme a total of 640 filters were analysed.

The random uncertainty of a single result obtained by the parallel measurements was calculated for each sampler at one sampling site as the standard deviation according to the following set of equations:

$$\bar{x}_d = \frac{\sum_{i=1}^M x_{id}}{M} \quad (5)$$

$$d_{id} = x_{id} - \bar{x}_d \quad (6)$$

$$s_i = \sqrt{\frac{\sum_{d=1}^N (d_{id} - \bar{d}_i)^2}{N - 1}} \quad (7) \quad \text{where : } \bar{d}_i = \frac{\sum_{d=1}^N d_{id}}{N} \quad (8)$$

with :

$M$	number of parallel samplers (= 8)
$N$	number of sampling days at one site (= 20)
$x_{id}$	result of sampler i on day d
$\overline{x_d}$	mean concentration of one day determined across all laboratories
$d_{id}$	deviation of sampler i from the daily mean
$\overline{d_i}$	mean deviation for sampler i over the trial period (20 days)
$s_i$	standard deviation determined for sampler i at one sampling site

The **standard random uncertainty** of the mean value for sampler i is calculated as the standard error:

$$u_{r,i} = \frac{s_i}{\sqrt{N}} \quad (9)$$

### 3.2.2.3 Non-Random Uncertainty

In addition to the random uncertainty estimated above it is necessary to take non-random contributions into account.

WG 14 agreed to determine the non-random uncertainty of the reference method using the results of the laboratory and field tests, both part of the Minimum Validation Programme. The following sources have been taken into account:

$$u_{nr} = \sqrt{u_{vol}^2 + u_{nra}^2} \quad (10)$$

where

$u_{vol}$	uncertainty of the sampling volume
$u_{nra}$	non-random uncertainty caused by the analytical step

#### 3.2.2.3.1 Uncertainty of the sampling volume

The bias of the sampling volume can be considered as a type B uncertainty with rectangular distribution. This bias is limited to 5 % according to the minimum requirements that have been established by WG 14.

The uncertainty contribution of the volume is then given as follows :

$$u_{vol} = \frac{5\%}{\sqrt{3}} = 2.9\% \quad (11)$$

### 3.2.2.3.1 Non Random Uncertainty of the analysis step

The certified reference material NIST SRM 1648 was digested and analysed following the procedure described by WG 14. The mean recovery across all laboratories was found to be consistent with the stated uncertainties of the CRM. The previous optimization of the method was successful.

The deviation of the mean concentration of one laboratory to the mean concentration that was determined across all laboratories is the remaining bias of that laboratory. However, the mean of all laboratories can only be compared to certified values carrying themselves an **uncertainty**  $u_{CRM}$ .

Therefore, the following equation is applied:

$$u_{nra,i} = \sqrt{\bar{d}_i^2 + u_{CRM}^2} \quad (12)$$

with

$u_{nra,i}$  **non-random uncertainty** of one laboratory caused by the analytical step

### 3.2.2.4 Combined Standard Uncertainty

The **Combined Standard Uncertainty** was calculated for each sampler at each sampling site

$$u_{c,i} = \sqrt{u_{r,i}^2 + u_{vol}^2 + u_{nra,i}^2} \quad (13)$$

### 3.2.2.5 Average of the Combined Standard Uncertainties

The **combined standard uncertainties** of all samplers have been averaged as best estimation of the combined uncertainty at one sampling site, corresponding to the particular level of heavy metal concentration at that site:

$$u_c = \frac{\sum_{i=1}^M u_{c,i}}{M} \quad (14)$$

### 3.2.2.6 Extrapolation of the Combined Uncertainty to the limit value

The averaged **combined standard uncertainties**  $u_c$  from all sampling sites, representing different concentration levels, were used to extrapolate and/or interpolate the uncertainty to the limit value. With help of the values for  $u_c$  a function for each element was found that is considered best estimation. As expected in most cases the function is linear when the uncertainty is expressed in absolute units.

After extrapolation,  $u_{c,lim}$  is then the **combined uncertainty at the limit value**.

### 3.2.2.7 Expanded Uncertainty

The **Expanded Uncertainty (overall uncertainty)** was then calculated using a coverage factor  $k$  as described in the GUM, corresponding to a level of confidence of about 95 %:

$$U = k * u_{c,lim} \quad (15)$$

As the data set at each site comprises 20 days sampling the factor  $k$  is set to  $k_{95} = 2.1$  for  $n = 20$  ( $f = 19$ ).

## 3.3 Uncertainty Results

According to the statistical procedure described above the uncertainty of both techniques AAS and ICP-MS was calculated.

Tables 6 and 7 contain the results of this calculation in more detail than shown in section 2. The standard uncertainties for each site and each laboratory are described as well as the combined standard uncertainty and the extrapolated or interpolated Expanded Uncertainty.

All original data (concentrations, blanks, recovery rates, sampling criteria) are documented in the annex of this report.

**Table 6: Summary of Combined and Expanded Uncertainties (AAS – Technique)**

<b>AAS - Technique</b>		<b>Combined Standard Uncertainties in (%)</b>								Mean of Comb. Uncert. (%)	Mean Conc. (ng/m <sup>3</sup> )	Abs.Unc (ng/m <sup>3</sup> )	Expanded Uncert. (%)
<b>Element Lead</b>	<b>Sampler No.</b>	Lab A/Q 1/1/1/1	Lab A/Q (Lab B/M 2/2/2/2	Lab B/M 8/3/3/3	Lab B/M 10/4/4/4	Lab C /M 5/5/5/5	Lab C /M 7/6/6/6	Lab D /Q 3/8/7/7	Lab D /Q 4/10/8/8				
Madrid		6	8	4	5	6	5	5	4	5	25	1	<b>7</b>
Bristol		4	3	3	6	4	6	6	5	5	85	4	
Berlin		4	5	5	5	6	11	3	6	6	26	1	
Antwerp		3	3	3	3	3	3	5	3	3	944	32	
<b>Cadmium</b>		Lab A/Q	Lab A/Q (Lab B/M	Lab B/M	Lab C /M	Lab C /M	Lab D /Q	Lab D /Q (A)					
Madrid		11	21	9	12	18	17	7	16	14	0,35	0,05	<b>13</b>
Bristol		6	6	6	6	7	8	8	6	7	3,78	0,25	
Berlin		15	20	20	6	8	12	8	6	12	0,36	0,04	
Antwerp		6	6	6	8	6	7	6	6	6	9,30	0,57	
<b>Arsenic</b>		Lab A/Q	Lab A/Q (Lab B/M	Lab B/M	Lab C /M	Lab C /M	Lab D /Q	Lab D /Q (A)					
Madrid		29	37	12	8	31	36	9	8	21	0,7	0,1	<b>18</b>
Bristol		8	13	9	10	9	12	7	6	9	1,7	0,2	
Berlin		7	8	7	9	6	6	5	6	7	3,3	0,2	
Antwerp		11	12	7	6	7	7	6	9	8	82,8	6,7	
<b>Nickel</b>		Lab A/Q	Lab A/Q (Lab B/M	Lab B/M	Lab C /M	Lab C /M	Lab D /Q	Lab D /Q (A)					
Madrid		24	76	53	62	70	30	54	17	48	1,5	0,7	<b>21</b>
Bristol		26	22	36	12	8	8	13	14	17	4,0	0,7	
Berlin		51	57	13	29	33	25	7	13	29	3,6	1,0	
Antwerp		7	11	20	15	6	9	6	13	11	15,8	1,7	

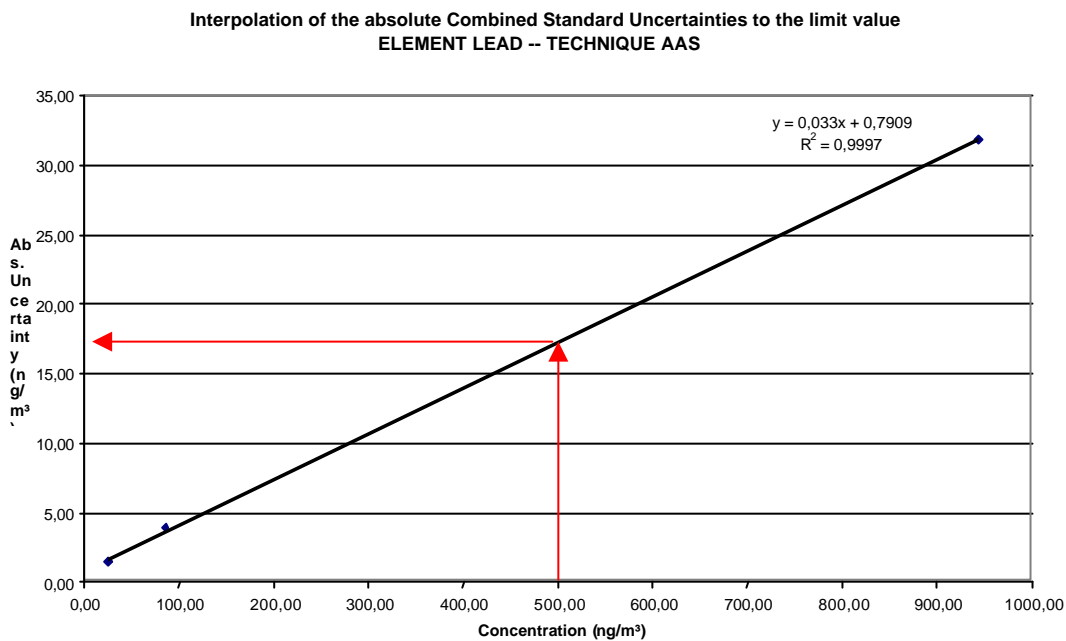
Table 7: Summary of Combined and Expanded Uncertainties (ICP-MS – Technique)

ICP-MS - Technique		Combined Standard Uncertainties in (%)							
Lead	Lab B/M (ICP)	Lab B/M (ICP)	Lab D /Q (ICP)	Lab D /Q (ICP)	Mean of Comb.	Mean Conc.	Abs.Unc	Expanded	
Sampler No.	8/3/3/3	10/4/4/4	3/8/7/7	4/10/8/8	Uncert. (%)	(ng/m³)	(ng/m³)	Uncert. (%)	
Madrid	7	11	9	10	9	26	2	12	
Bristol	5	4	6	3	5	85	4		
Berlin	6	8	12	3	7	25	2		
Antwerp	6	6	4	8	6	870	51		
Cadmium									
	Lab B/M (ICP)	Lab B/M (ICP)	Lab D /Q (ICP)	Lab D /Q (ICP)					
Madrid	18	8	15	13	13	0,35	0,05	17	
Bristol	10	8	6	7	8	4,05	0,32		
Berlin	11	12	8	6	9	0,40	0,04		
Antwerp	6	9	6	9	8	8,90	0,69		
Arsenic									
	Lab B/M (ICP)	Lab B/M (ICP)	Lab D /Q (ICP)	Lab D /Q (ICP)					
Madrid	16	11	14	15	14	0,6	0,1	14	
Bristol	7	6	6	7	6	1,9	0,1		
Berlin	7	10	7	5	7	3,5	0,3		
Antwerp	7	6	8	5	6	89,4	5,7		
Nickel									
	Lab B/M (ICP)	Lab B/M (ICP)	Lab D /Q (ICP)	Lab D /Q (ICP)					
Madrid	42	20	35	12	27	1,0	0,3	9	
Bristol	24	14	36	8	20	3,0	0,6		
Berlin	21	27	35	14	24	3,4	0,8		
Antwerp	5	4	4	6	5	14,7	0,7		

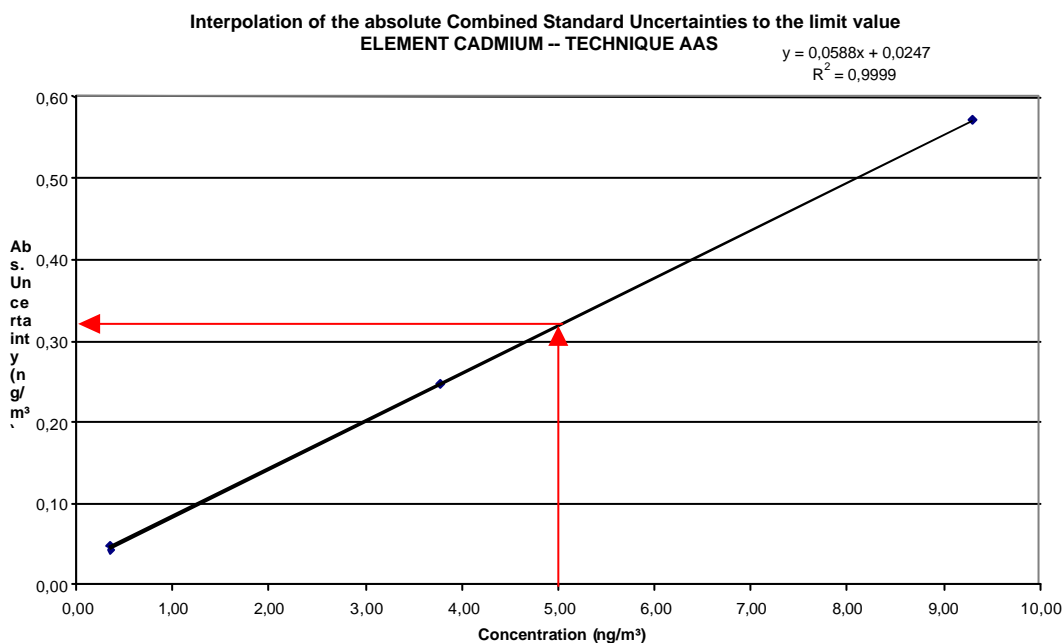
### 3.4 Extrapolations / Interpolations

The following diagrams show how the extrapolations or interpolations of the **Combined Standard Uncertainties** were performed to calculate the **Uncertainty at the limit value**. For this the averaged Combined Uncertainties for each sampling site are drawn into a diagram. The **Combined Standard Uncertainty at the limit value** was calculated with the help of the linear regression function as best fit.

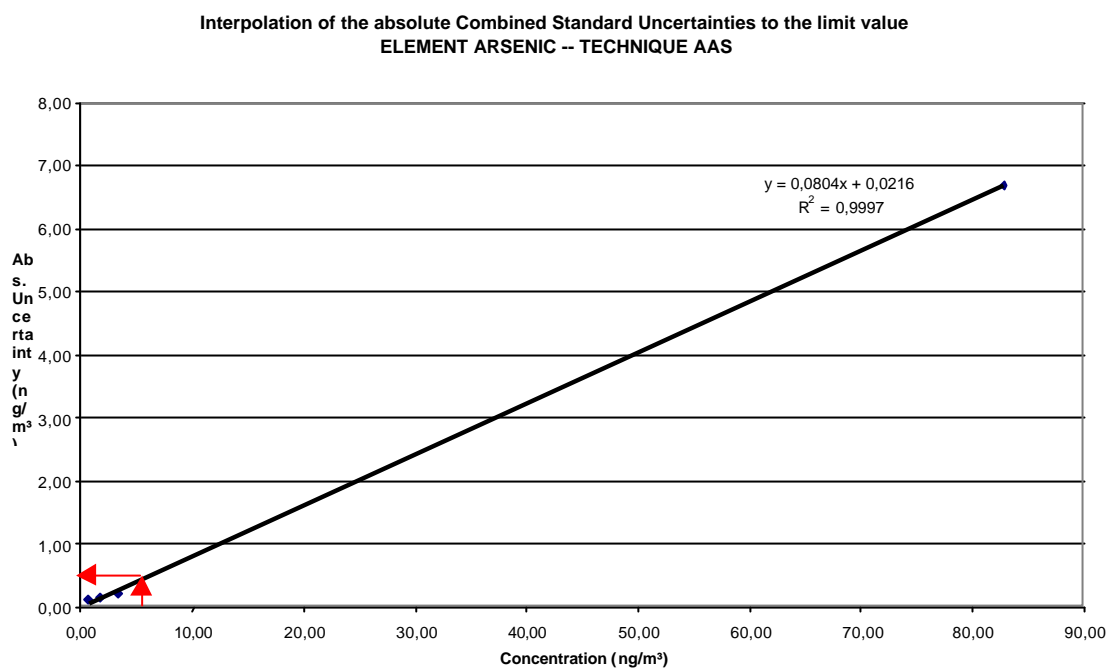
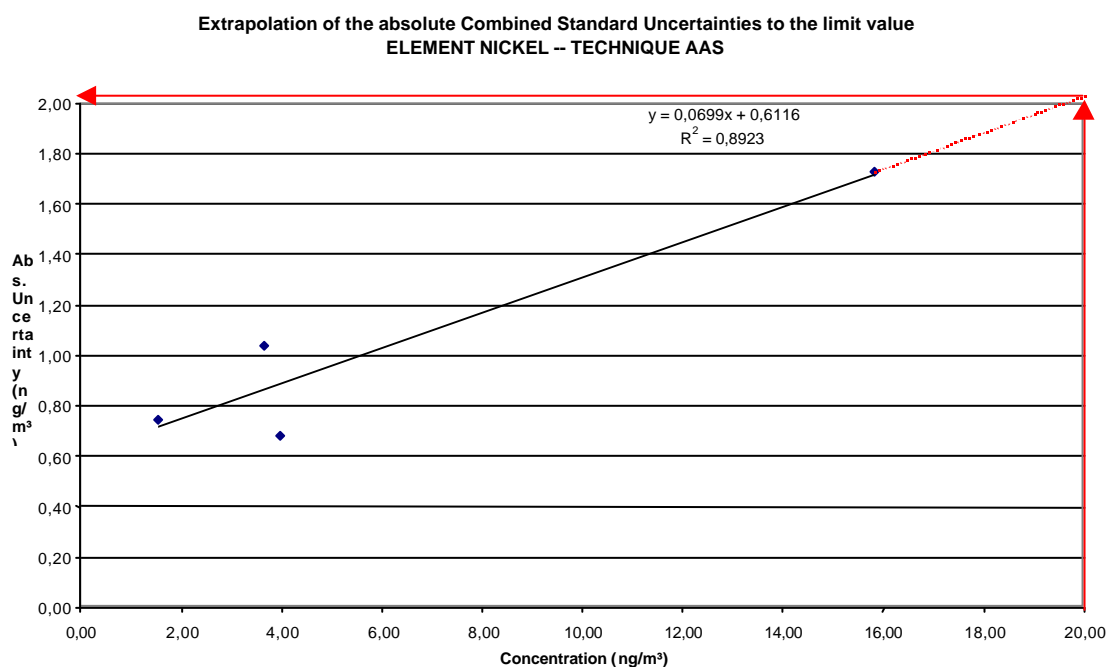
**Diagram 1: Lead with AAS – Technique**

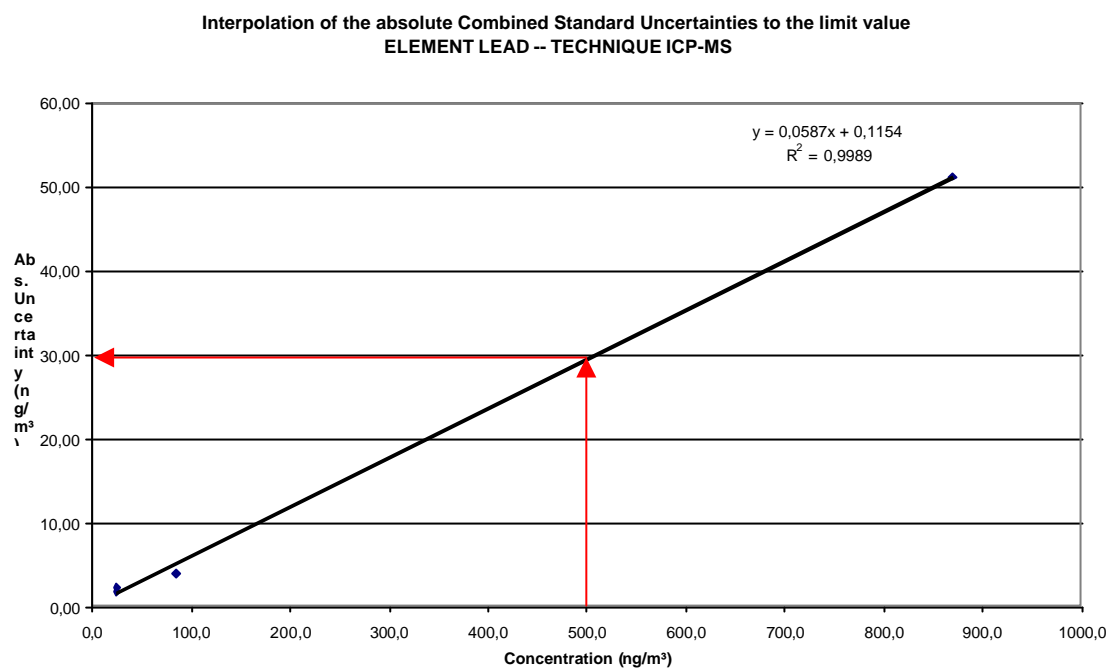
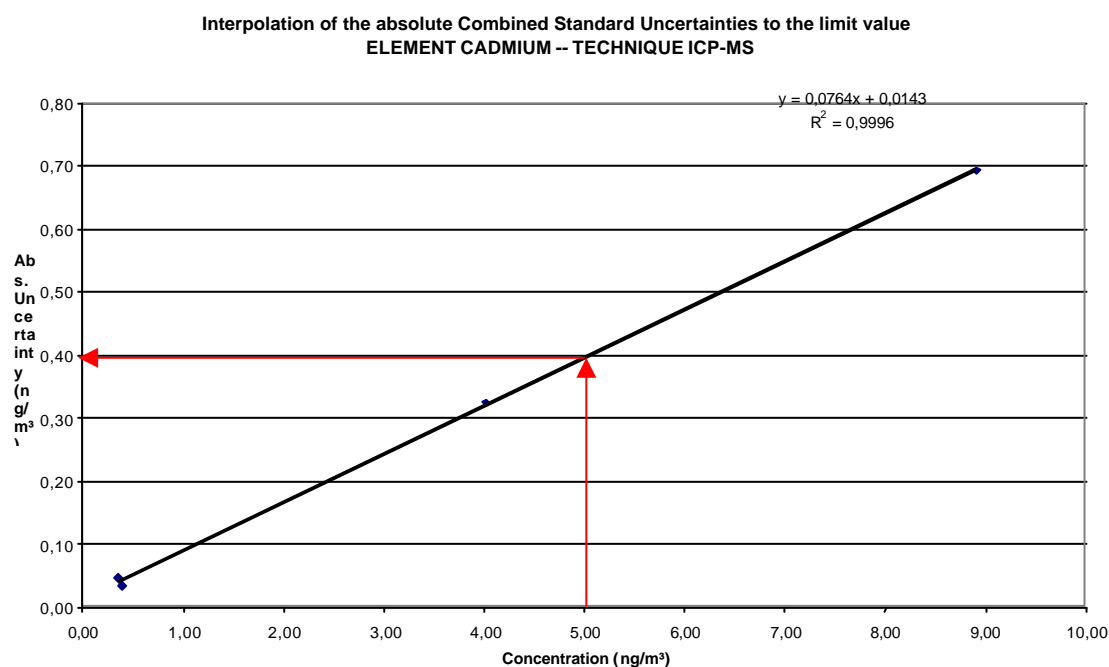


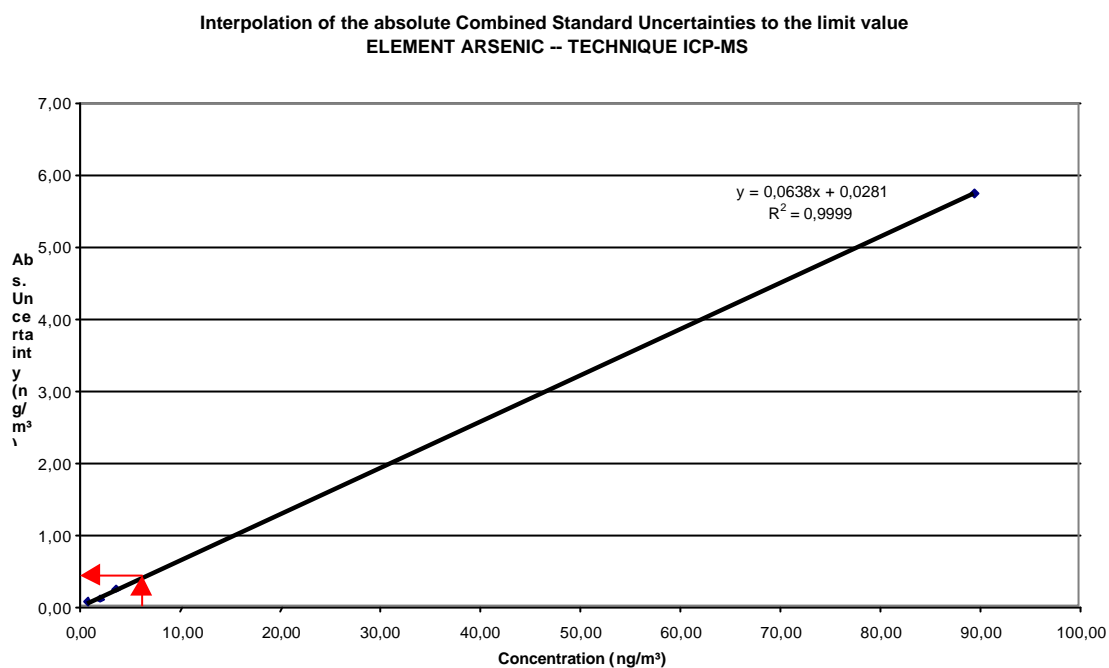
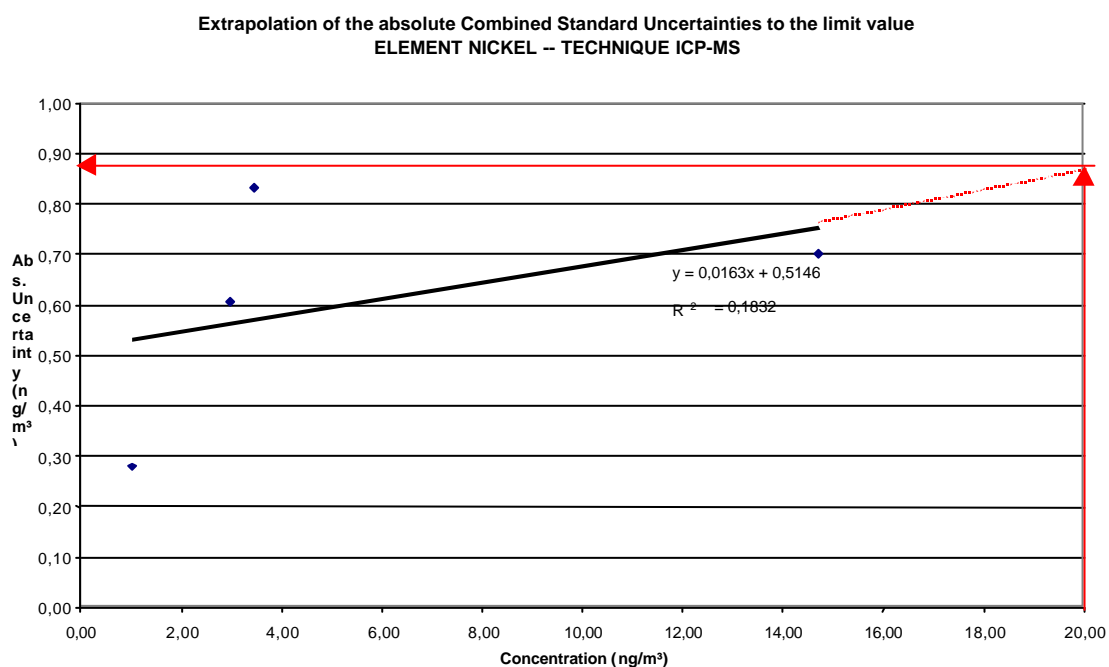
**Diagram 2: Cadmium with AAS – Technique**





**Diagram 3: Arsenic with AAS – Technique****Diagram 4: Nickel with AAS – Technique**

**Diagram 5: Lead with ICP-MS – Technique****Diagram 6: Cadmium with ICP-MS – Technique**

**Diagram 7: Arsenic with ICP-MS – Technique****Diagram 8: Nickel with ICP-MS – Technique**

### 3.5 Interpretation of the results

The results shown in Tables 11 and 12 show that both techniques of the Reference Method of WG14 meet the requirements (see also Table 1).

Diagrams 1 to 7 show that the correlations between the calculated absolute combined uncertainties and the mean concentration can be described very well with a linear function. For the elements Lead, Cadmium and Arsenic, this gives a good correspondence with  $R^2$  values better than 0.99. The Nickel correlation for the AAS data set is acceptable with an  $R^2 = 0.89$ .

Diagram 8 shows the Nickel correlation for ICP-MS. Here only an  $R^2$  of 0.18 could be achieved. The reason for this is the better quality of the analysis at the site Hoboken (Antwerp), which - with a mean concentration of  $14.7 \text{ ng/m}^3$  - is nearest to the limit value of  $20 \text{ ng/m}^3$ . Obviously a better uncertainty was achieved because of an improvement of the ICP-MS laboratories.

The determined Expanded Uncertainties for Cadmium (17.6 % AAS / 14.4 % ICP) and Arsenic (13.4 % AAS / 16.6 % ICP) are in the same range for both analytical techniques.

For the element Lead the AAS Uncertainty at 7.3 % is lower than the Uncertainty of 12.4 % of the ICP-MS.

In contrast to that the AAS Uncertainty for Nickel at 21.1 % is significantly higher than the Uncertainty of the ICP-MS data set of 8.8 %.

When these results are considered it must be taken into account that the ICP-MS data set was only constructed with four samples (two laboratories) per day, in comparison to the AAS data set. Here 8 samples (four laboratories) per day were investigated.

In section 5 an evaluation is included which shows more aspects related to the different sampling sites.

## 4 Further statistical evaluation of the data sets

In addition to the uncertainty results discussed above some other statistical calculations were performed. These evaluations complement the performance characteristics that have already been shown in the sections above.

The additional calculations are the Detection limits, Recovery rates, Repeatability and Reproducibility as well as correlation examinations for AAS compared with ICP-MS and Quartz fibre filter compared with Membrane filters.

#### 4.1 Detection Limit

During the Field Validation Programme the Lab filter blanks were determined in order to calculate the Detection Limit of the method.

The following equations (16) and (17) show the calculation :

$$s_{LB} = \sqrt{\frac{\sum_{i=1}^n (\bar{x} - x_i)^2}{n-1}} \quad (16) \quad \text{and} \quad LoD_M = t_{f=15,P} * s_B \quad (17)$$

Where:

$LoD_M$  = Detection Limit of the Method

$s_{LB}$  = Standard Deviation of the Lab Filter Blanks

$n$  = Number of the Lab Filter Blanks

$x_i$  = Concentration of the Lab Filter Blank solution

$t_{15,95}$  = 2.13 (Student's factor for  $n=16$  and  $P=95\%$  ;  $f=n-1$ )

$t_{15,99}$  = 2.95 (Student's factor for  $n=16$  and  $P=99\%$  ;  $f=n-1$ )

The Detection Limits based on the Lab filter blanks are calculated for a probability of  $P=95\%$  as well as for  $P=99\%$  in  $ng/m^3$  for a theoretical volume of  $55 m^3$ .

**Table 8: Detection Limit based on filter blanks for the AAS technique**

Detection limits in $ng/m^3$					
	Probability	Lead	Cadmium	Arsenic	Nickel
Lab A	95 %	0,7	0,11	0,5	1,1
	99 %	1,0	0,15	0,7	1,6
Lab B	95 %	1,3	0,16	0,3	1,3
	99 %	1,9	0,22	0,4	1,8
Lab C	95 %	0,5	0,05	0,2	1,1
	99 %	0,6	0,07	0,3	1,5
Lab D	95 %	0,6	0,03	0,2	1,1
	99 %	0,8	0,04	0,3	1,5

**Table 9: Detection Limit based on filter blanks for the ICP-MS technique**

Detection limits in $ng/m^3$					
	Probability	Lead	Cadmium	Arsenic	Nickel
Lab B	95 %	0,9	0,70	0,2	1,3
	99 %	1,3	0,98	0,2	1,8
Lab D	95 %	2,1	0,08	0,4	1,3
	99 %	2,9	0,11	0,6	1,8

## 4.2 Recovery Rate

The Recovery rates were checked using both certified reference materials NIST 1648 and NIES No.8. The material with the higher priority was the NIST CRM because its consistence is similar to the matrix of real dusts in ambient air. Moreover it is widely available.

The NIES No.8 material was placed at our disposal in the framework of a research project.

The Recovery Rate (in %) was calculated according to the following equation (18). Tables 10 to 13 show the results.:

$$R_r = \frac{x_a}{x_c} * 100 \quad (18)$$

where :

$R_r$  : Recovery Rate (%)  
 $x_c$  : Certified concentration of the CRM  
 $x_a$  : Concentration found in the analysis of the CRM

**Table 10: Recovery Rate for NIST 1648 (AAS technique)**

		Recovery Rates in %			
		Lead	Cadmium	Arsenic	Nickel
Lab A	Mean	98	95	103	93
	RSD	2	3	3	4
Lab B	Mean	103	98	107	98
	RSD	5	13	6	8
Lab C	Mean	99	96	105	96
	RSD	4	5	5	6
Lab D	Mean	99	97	110	99
	RSD	4	7	3	5
<b>Total Mean</b>		<b>100</b>	<b>97</b>	<b>106</b>	<b>96</b>
<b>Certificate</b>		<b>99 - 101</b>	<b>91 - 109</b>	<b>93 - 109</b>	<b>96 - 104</b>

**Table 11: Recovery Rate for NIST 1648 (ICP-MS technique)**

		Recovery Rates in %			
		Lead	Cadmium	Arsenic	Nickel
Lab B	Mean	98	103	109	98
	RSD	5	6	5	6
Lab D	Mean	98	98	107	96
	RSD	7	9	7	8
<b>Total Mean</b>		<b>98</b>	<b>101</b>	<b>108</b>	<b>97</b>
<b>Certificate</b>		<b>99 - 101</b>	<b>91 - 109</b>	<b>93 - 109</b>	<b>96 - 104</b>

**Table 12: Recovery Rate for NIES No.8 (AAS technique)**

Recovery Rates in %					
		Lead	Cadmium	Arsenic	Nickel
Lab A	Mean	103	96	109	92
	RSD	2	4	5	3
Lab B	Mean	107	94	85	93
	RSD	9	19	7	7
Lab C	Mean	100	94	106	97
	RSD	5	6	6	8
Lab D	Mean	101	89	126	96
	RSD	3	8	7	11
<b>Total Mean</b>		<b>103</b>	<b>93</b>	<b>106</b>	<b>94</b>
<b>Certificate</b>		<b>96 - 104</b>	<b>91 - 109</b>	<b>92 - 108</b>	<b>92 - 108</b>

**Table 13: Recovery Rate for NIES No.8 (ICP-MS technique)**

Recovery Rates in %					
		Lead	Cadmium	Arsenic	Nickel
Lab B	Mean	100	100	112	91
	RSD	3	14	7	8
Lab D	Mean	103	102	126	95
	RSD	4	10	9	9
<b>Total Mean</b>		<b>102</b>	<b>101</b>	<b>119</b>	<b>93</b>
<b>Certificate</b>		<b>96 - 104</b>	<b>91 - 109</b>	<b>92 - 108</b>	<b>92 - 108</b>

### 4.3 Repeatability and Reproducibility

For the determination of Repeatability and Reproducibility the 20 days sampling period at each site was taken as a basis.

Repeatability is the scattering of the method when it is applied by one laboratory expressed as the standard deviation of the samples of two parallel operated samplers.

The Repeatability  $r$  is calculated as follows:

$$r = \sqrt{\frac{\sum_{i=1}^N (x_1 - x_2)^2}{2N}} \quad (19)$$

with :

$x_1, x_2$  : Results of the parallel sampled filters

$N$  : Number of days (=20)

$r$  : Repeatability of one laboratory at one sampling site

Reproducibility is the scattering of the method when it is applied by several laboratories expressed as the standard deviation across all samplers.

The Reproducibility R is calculated as follows:

$$R = \sqrt{\frac{\sum_{i=1}^N \left( \sum_{k=1}^M (x_{i,k} - \bar{x}_i)^2 \right)}{(N * M) - N}} \quad (20)$$

with :

$x_{i,k}$  : Result of sampler k on day i

N : Number of days

M : Number of parallel samplers

R : Reproducibility across all samplers (labs) at one sampling site

#### 4.4 Results of Repeatability and Reproducibility

Tables 14 and 15 list the Repeatability and Reproducibility for the two analytical techniques GF-AAS and ICP-MS.

Table 14: Repeatability and Reproducibility with GF-AAS

AAS - technique		Relative Repeatability (%)								Mean Repeatability (%)	Reproducibility (%)	Mean conc ng/m³
Lead	Sampler No.	Lab A/Q		Lab B/M (A)		Lab C /M (A)		Lab D /Q (A)				
		1/1/1/1	2/2/2/2	8/3/3/3	10/4/4/4	5/5/5/5	7/6/6/6	3/8/7/7	4/10/8/8			
	Madrid	10		10		5		7		8	9	25
	Bristol	2		9		3		8		5	8	85
	Berlin	2		12		7		6		7	10	26
	Antwerp	2		5		3		5		4	4	944
Cadmium		Lab A/Q		Lab B/M (A)		Lab C /M (A)		Lab D /Q (A)				
	Madrid	19		26		6		48		25	34	0,35
	Bristol	3		9		3		16		8	10	3,78
	Berlin	12		14		8		7		10	19	0,36
	Antwerp	3		6		3		7		5	7	9,30
Arsenic		Lab A/Q		Lab B/M (A)		Lab C /M (A)		Lab D /Q (A)				
	Madrid	31		17		10		12		18	37	0,7
	Bristol	13		27		6		15		15	22	1,7
	Berlin	13		9		2		4		7	16	3,3
	Antwerp	3		7		2		12		6	13	82,8
Nickel		Lab A/Q		Lab B/M (A)		Lab C /M (A)		Lab D /Q (A)				
	Madrid	82		124		85		82		93	94	1,5
	Bristol	10		62		22		49		36	41	4,0
	Berlin	13		16		37		21		22	40	3,6
	Antwerp	16		12		13		19		15	21	15,8

\* Repeatability averaged across all laboratories



Table 15: Repeatability and Reproducibility with ICP-MS

ICP-MS - Technique		Relative Repeatability (%)				Mean Repeatability* (%)	Reproducibility (%)	Mean concentration/m³
Lead	Lab B/M	Lab D/Q						
Sampler ....	1/1/1/1	2/2/2/2	8/3/3/3	10/4/4/4				
Madrid	10		22		16	18	25	
Bristol	7		12		9	10	85	
Berlin	9		10		9	11	26	
Antwerp	5		5		5	9	944	
Cadmium								
	Lab B/M	Lab D/Q						
Madrid	33		58		45	41	0,35	
Bristol	28		13		21	24	3,78	
Berlin	18		16		17	16	0,36	
Antwerp	8		6		7	14	9,30	
Arsenic								
	Lab B/M	Lab D/Q						
Madrid	7		38		23	28	0,7	
Bristol	8		13		10	12	1,7	
Berlin	15		7		11	12	3,3	
Antwerp	4		7		5	7	82,8	
Nickel								
	Lab B/M	Lab D/Q						
Madrid	105		70		88	89	1,5	
Bristol	28		43		35	46	4,0	
Berlin	21		30		25	37	3,6	
Antwerp	9		7		8	9	15,8	

\* Repeatability averaged across all laboratories

As expected the Repeatability for all sampling sites and elements is lower than the Reproducibility. This is because the Repeatability is only dependent on one laboratory. In contrast to this the Reproducibility is influenced by the deviations of all laboratories.

In comparison with the Uncertainty the Repeatability and Reproducibility values are higher. The reason is that the Uncertainty is expressed as a performance characteristic for the whole data set of one sampling site. The Repeatability and Reproducibility are criteria for a single value and not for a data set.

## 4.5 Correlations

There are several possibilities to compare data sets acquired in parallel, that originate for example from different laboratories or analysis techniques.

One way is the  $t$ -test of differences, where the mean and the standard deviation of the differences between two data series are compared according to the following equation:

$$tv = \frac{|\overline{d}|}{s} * \sqrt{n} \quad (21)$$

where :

tv : Test value

$|\overline{d}|$  : Mean of differences

s : Standard deviation of differences

n : Number of pairs

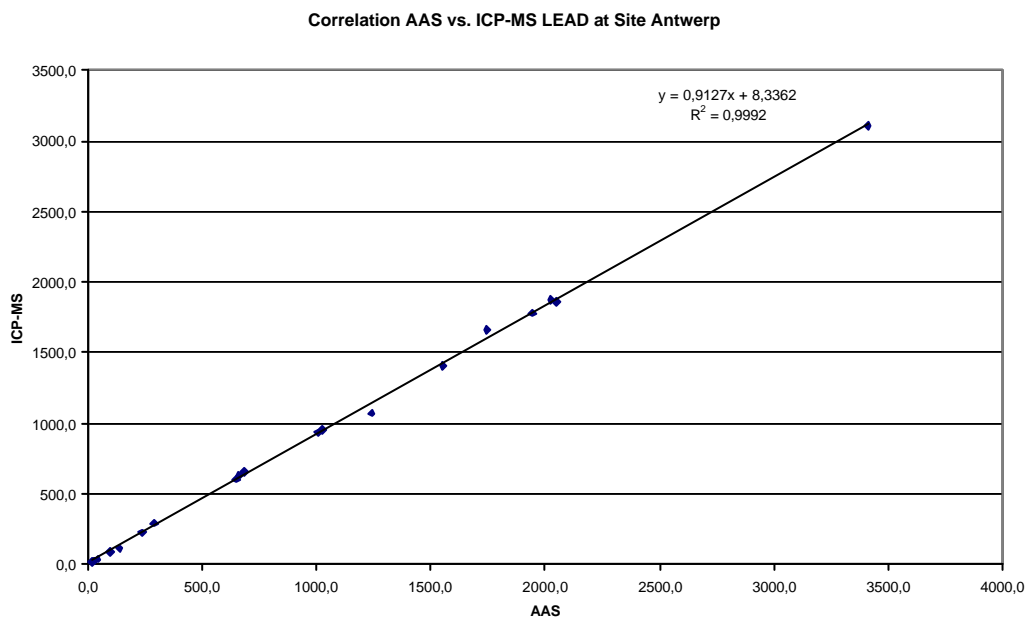
The value tv is compared with the student's factor  $t_{f,p}$ . Usually  $p=99\%$  is applied to get information as to whether the data series are significantly different or not. In practice this test often shows significant differences as a result when the standard deviation of the differences are very small. In cases when the Reproducibility is very high the test is too rigorous.

Correlation diagrams between different data series are a better option to illustrate results in a very clear form. In the following section such diagrams were created to compare the AAS with the ICP-MS technique and the Quartz fibre filters with the Membrane filters.

#### 4.5.1 Comparison AAS versus ICP-MS

The following diagram shows the results of both techniques in x-y-diagrams for the element Lead at the sampling site Antwerp as an example. The concerning regression function and the correlation expressed as  $R^2$  are shown in the diagram.

**Diagram 9: Correlation for Lead at the site Antwerp**



All 16 diagrams for the 4 sampling sites and 4 elements are included in Annex D.

The diagrams show that the correlations almost correspond between AAS and ICP-MS technique apart from for the element Nickel. Slopes are in most cases between 0.9 and 1.1. Here again it can be seen that the Antwerp data set has the best quality because of the higher concentrations and the experience gathered during the MVP.

In contrast to that the Madrid data set shows higher scattering and more deviation from the ideal function  $x=y$  because of very low concentrations.

For the element Nickel in particular higher deviations were discovered. Only in the Antwerp data set was a good correlation of  $R^2=0.9919$ , a slope of 1.001 and an offset of  $-1.13$  found. The negative offset can be related to the fact that because of the higher detection limit the AAS results contain a certain - but small - uncorrected blank value.

#### **4.5.2 Comparison Quartz versus Membrane filters**

The Diagrams in Annex E show the results of Quartz and Membrane filters in an x-y-diagram. For this comparison only the data set of Antwerp (AAS technique) was investigated, because this is the most robust data set as already mentioned in the previous section.

As the diagrams show, there are very good correlations between the analytical results with Quartz and Membrane filters.

The slope for Lead, Cadmium and Arsenic is close to 1. That means that there is no significant difference between both data sets.

For Nickel a small difference can be observed with a slope of 0.85 and an offset of 0.73. However, the deviation is not significant as when the highest concentration is eliminated then the slope is 0.91 and the offset  $-1.1$ .

## **5 Site characterization**

The four sampling sites were selected to get a wide range of different concentrations and different sources for the PM10-Particles such as traffic and industry.

In this section a short characterization of the four sampling sites is given, taking the results into account. A detailed description of the sampling sites is given in the site reports of the Field Test.

### 5.1 Sampling site: Madrid

The first sampling site was in Madrid. This urban sampling site is mainly influenced by traffic. The sampling period was from 04.05.-25.05.2001.

The site Madrid showed due to meteorological conditions the lowest concentration for all elements, so that the uncertainty measurement was found to be the highest.

**Table 16** shows the mean concentrations for all elements:

Element	Mean conc (ng/m <sup>3</sup> )	Min. conc (ng/m <sup>3</sup> )	Max. conc (ng/m <sup>3</sup> )	Stand. dev. of conc. (ng/m <sup>3</sup> )	Exp. Uncer- tainty (%)	Reproduci- bility (%)
Lead	25.3	7.6	44	9.26	12	9
Cadmium	0.35	0.01	1.2	0.31	28	34
Arsenic	0.65	0.05	2.1	0.31	42	37
Nickel	1.53	0.35	8.8	0.90	98	94

### 5.2 Sampling site: Avonmouth

The second sampling site was in Avonmouth, an industrial site near Bristol. The sampling period was from 08.07.-02.08.2001.

The mean concentrations for the elements Lead, Cadmium and Nickel were the second highest of all sampling sites.

**Table 17** shows the mean concentrations for all elements:

Element	Mean conc (ng/m <sup>3</sup> )	Min. conc (ng/m <sup>3</sup> )	Max. conc (ng/m <sup>3</sup> )	Stand. dev. of conc. (ng/m <sup>3</sup> )	Exp. Uncer- tainty (%)	Reproduci- bility (%)
Lead	85.4	2.8	469	86.0	9	8
Cadmium	3.78	0.02	28.6	4.25	13	10
Arsenic	1.66	0.07	10.8	1.34	19	22
Nickel	3.97	0.22	8.8	1.78	34	41

### 5.3 Sampling site: Berlin

The third sampling site was in Berlin, an urban site fairly influenced by traffic. The sampling period was from 12.09.-15.10.2001.

The results for the elements Lead, Cadmium and Nickel are – as expected - small in comparison with the concentrations at the industrial sites in Antwerp and Bristol. Only for Arsenic was the mean value was higher than the one from Bristol. This was due to two days with concentrations that were ten times higher than the mean.

**Table 18** shows the mean concentrations for all elements:

Element	Mean conc (ng/m <sup>3</sup> )	Min. conc (ng/m <sup>3</sup> )	Max. conc (ng/m <sup>3</sup> )	Stand. dev. of conc. (ng/m <sup>3</sup> )	Exp. Uncer- tainty (%)	Reproduci- bility (%)
<b>Lead</b>	<b>26.3</b>	<b>9.3</b>	<b>90.8</b>	<b>16.5</b>	<b>11</b>	<b>10</b>
<b>Cadmium</b>	<b>0.36</b>	<b>0.01</b>	<b>1.2</b>	<b>0.22</b>	<b>24</b>	<b>19</b>
<b>Arsenic</b>	<b>3.30</b>	<b>0.07</b>	<b>29.8</b>	<b>6.91</b>	<b>13</b>	<b>16</b>
<b>Nickel</b>	<b>3,63</b>	<b>0.48</b>	<b>8.2</b>	<b>1.15</b>	<b>57</b>	<b>40</b>

#### 5.4 Sampling site: Antwerp

The fourth and last sampling site was an area in Hoboken by Antwerp, a site strongly influenced by industry. The sampling period was from 06.11.-16.12.2001.

For this site for all elements the highest concentrations were measured.

**Table 19** shows the mean concentrations for all elements:

Element	Mean conc (ng/m <sup>3</sup> )	Min. conc (ng/m <sup>3</sup> )	Max. conc (ng/m <sup>3</sup> )	Stand. dev. of conc. (ng/m <sup>3</sup> )	Exp. Uncer- tainty (%)	Reproduci- bility (%)
<b>Lead</b>	<b>944</b>	<b>20.5</b>	<b>3530</b>	<b>946</b>	<b>7</b>	<b>4</b>
<b>Cadmium</b>	<b>9.30</b>	<b>0.51</b>	<b>28.4</b>	<b>9.0</b>	<b>12</b>	<b>7</b>
<b>Arsenic</b>	<b>82.8</b>	<b>1.09</b>	<b>325</b>	<b>82.4</b>	<b>16</b>	<b>13</b>
<b>Nickel</b>	<b>15.8</b>	<b>2.81</b>	<b>63.7</b>	<b>12.5</b>	<b>21</b>	<b>21</b>

Due to the very high concentrations during the field trial in Antwerp, it was possible to acquire data that lead to a robust extrapolation or interpolation of the Uncertainties to the limit value.

The mean concentrations of Lead, Cadmium and Arsenic were above the (proposed) limit values. The concentration for Nickel came up to about 80 % of the proposed limit value.

## 6 Summary

The task of WG 14 is to work out the CEN Standard “Air Quality – Reference Method for the measurement of Pb/Cd/As/Ni in ambient air for the implementation of EC Air Quality Directives”.

A measurement method on the basis of PM10-Sampling, a microwave digestion procedure and the analytical techniques GF-AAS respective ICP-MS has therefore been developed.

A major part of the work of WG 14 has been the validation of this new Reference method. For this a Minimum Validation Programme (MVP) was specified. This MVP comprised both laboratory and field validation work.

The 4 different phases of that MVP were :

- Laboratory Tests
- Preparation of Field Tests
- Preliminary Field Tests
- Field Validation Programme (FVP)

The FVP was carried out at four sampling sites in Europe (Madrid, Bristol, Berlin and Antwerp) within one year. At each sampling site 8 samplers were operated for 20 days in parallel. At the end a total of 640 samples were available. The analysis of the filters was performed by four laboratories using AAS technique and two laboratories using ICP-MS technique. All parts of the MVP have been documented in accompanying reports.

The results of the FVP were the basis for several calculations as described in this report :

- Expanded Uncertainty (acc. to the GUM)
- Repeatability
- Reproducibility
- Comparisons between AAS/ICP-MS
- Comparisons between filter materials

For the evaluation of the Expanded Uncertainty, WG 14 has developed a statistical model according to the GUM (see section 3). In the first step all uncertainty contributions were taken into account in order to evaluate the Combined Standard Uncertainties for all laboratories at the various sampling sites. In a second step the calculated and averaged Combined Uncertainties were used to extrapolate or interpolate the results to the limit value as required.

The results show that the requirements regarding the (proposed) measurement uncertainties of the 1<sup>st</sup> Daughter Directive and the Position Paper on Cadmium, Arsenic and Nickel have been fulfilled.

# ANNEX

## **Annex A: Bibliography**

- [1] 1<sup>st</sup> Daughter Directive, 1999/30/EG
- [2] Position Paper on Cadmium, Arsenic and Nickel
- [3] GUM – Guide to the expression of Uncertainty in measurements, ISO
- [4] Terms of Reference, CEN TC264
- [5] Approach to Uncertainty Estimation, CEN TC264 ad-hoc WG

**Annex B : Blank Correction**

**Annex C : Outlier Correction**

**Annex D : Comparison between GF-AAS and ICP-MS**

**Annex E : Comparison between Quartz- and Membrane filters**

## Annex B: Blank Correction

Tables B1 to B6 show the limits of detection and the determined lab filter blanks for all participating laboratories.

**Table B1: Blanks for laboratory A (technique AAS)**

CEN TC 264/WG 14								
Calculation of the detection limits and blank correction								
Lab A (AAS)								
Reagent Blanks (ng/m <sup>3</sup> )	Blanks and it's correction in ng/m <sup>3</sup>							
Elements	Lead	Correction	Cadmium	Correction	Arsenic	Correction	Nickel	Correction
Mean ng/m <sup>3</sup>	0.95		-0.01		-1.53		0.66	
SD ng/m <sup>3</sup>	0.23		0.01		1.33		0.17	
3*SD=LoD	0.68		0.02		4.00		0.52	
Filter-Blank Madrid	0.36		-0.03		-0.04		1.34	1.34
Filter-Blank Bristol	0.24		0.06	0.06	0.03		0.48	
Filter-Blank Berlin	0.24		0.06	0.06	0.03		0.48	
Filter-Blank Antwerp	0.81	0.81	-0.04		-0.13		1.09	1.09

**Table B2: Blanks for laboratory B (technique AAS)**

CEN TC 264/WG 14								
Calculation of the detection limits and blank correction								
Lab B (AAS)								
Reagent Blanks (ng/m <sup>3</sup> )	Blanks and it's correction in ng/m <sup>3</sup>							
Elements	Lead	Correction	Cadmium	Correction	Arsenic	Correction	Nickel	Correction
Mean ng/m <sup>3</sup>	-1.33		0.08		0.03		-0.28	
SD ng/m <sup>3</sup>	0.31		0.03		0.13		0.23	
3*SD=LoD	0.93		0.09		0.39		0.69	
Filter-Blank Madrid	0.30		0.04		0.00		1.37	1.37
Filter-Blank Bristol	1.16	1.16	0.02		-0.24		0.62	
Filter-Blank Berlin	-0.01		0.00		0.00		0.00	
Filter-Blank Antwerp	0.20		-0.09		0.00		-0.39	

**Table B3: Blanks for laboratory C (technique AAS)**

CEN TC 264/WG 14								
Calculation of the detection limits and blank correction								
Lab C (AAS)								
Reagent Blanks (ng/m <sup>3</sup> )	Blanks and it's correction in ng/m <sup>3</sup>							
Elements	Lead	Correction	Cadmium	Correction	Arsenic	Correction	Nickel	Correction
Mean ng/m <sup>3</sup>	0.02		0.03		-0.23		0.10	
SD ng/m <sup>3</sup>	0.80		0.01		0.04		0.15	
3*SD=LoD	2.41		0.02		0.13		0.46	
Filter-Blank Madrid	0.59		0.04	0.04	0.06		1.02	1.02
Filter-Blank Bristol	0.31		-0.01		-0.01		1.10	1.10
Filter-Blank Berlin	0.36		0.01		-0.13		1.16	1.16
Filter-Blank Antwerp	0.35		0.02	0.02	-0.01		0.46	0.46



**Table B4: Blanks for laboratory D (technique AAS)**

CEN TC 264/WG 14								
Calculation of the detection limits and blank correction								
Lab D (AAS)								
Reagent Blanks (ng/m <sup>3</sup> )	Blanks and it's correction in ng/m <sup>3</sup>							
Elements	Lead	Correction	Cadmium	Correction	Arsenic	Correction	Nickel	Correction
Mean ng/m <sup>3</sup>	0,26		0,02		0,09		0,65	
SD ng/m <sup>3</sup>	0,20		0,01		0,07		0,14	
3*SD=LoD	0,60		0,03		0,22		0,43	
Filter-Blank Madrid	0,83	0,83	-0,01		-0,14		1,62	1,62
Filter-Blank Bristol	0,69	0,69	0,01		-0,23		1,47	1,47
Filter-Blank Berlin	0,78	0,78	0,00		-0,07		0,85	0,85
Filter-Blank Antwerp	0,37		0,00		-0,16		0,91	0,91

**Table B5: Blanks for laboratory B (technique ICP-MS)**

CEN TC 264/WG 14								
Calculation of the detection limits and blank correction								
Lab B (ICP-MS)								
Reagent Blanks (ng/m <sup>3</sup> )	Blanks and it's correction in ng/m <sup>3</sup>							
Elements	Lead	Correction	Cadmium	Correction	Arsenic	Correction	Nickel	Correction
Mean ng/m <sup>3</sup>	0,20		0,02		0,16		0,45	
SD ng/m <sup>3</sup>	0,03		0,00		0,12		0,08	
3*SD=LoD	0,08		0,00		0,36		0,24	
Filter-Blank Madrid	0,30	0,30	0,02	0,02	0,20		0,82	0,82
Filter-Blank Bristol	0,89	0,89	0,38	0,38	0,16		1,01	1,01
Filter-Blank Berlin	0,00		0,00	0,00	0,00		0,01	
Filter-Blank Antwerp	0,38	0,38	0,01	0,01	0,15		0,31	0,31

**Table B6: Blanks for laboratory D (technique ICP-MS)**

CEN TC 264/WG 14								
Calculation of the detection limits and blank correction								
Lab D (ICP)								
Reagent Blanks (ng/m <sup>3</sup> )	Blanks and it's correction in ng/m <sup>3</sup>							
Elements	Lead	Correction	Cadmium	Correction	Arsenic	Correction	Nickel	Correction
Mean ng/m <sup>3</sup>	0,01		0,00		0,01		0,03	
SD ng/m <sup>3</sup>	0,00		0,00		0,03		0,00	
3*SD=LoD	0,01		0,00		0,09		0,01	
Filter-Blank Madrid	2,54	2,54	0,08	0,08	0,13	0,13	1,75	1,75
Filter-Blank Bristol	0,76	0,76	0,03	0,03	-0,01		1,60	1,60
Filter-Blank Berlin	0,95	0,95	0,02	0,02	0,08		0,73	0,73
Filter-Blank Antwerp	0,53	0,53	0,01	0,01	0,00		1,08	1,08

## Annex C: Outlier Correction

### Number of Outliers, Sampling Site Madrid:

Laboratory	Lead	Cadmium	Arsenic	Nickel
A (AAS)	1			3
B (AAS)		2		2
C (AAS)				5
D (AAS)	1			
B (ICP-MS)				1
D (ICP-MS)				1

### Number of Outliers, Sampling Site Bristol:

Laboratory	Lead	Cadmium	Arsenic	Nickel
A (AAS)	1	1		
B (AAS)		4		
C (AAS)				
D (AAS)				
B (ICP-MS)				1
D (ICP-MS)				3

### Number of Outliers, Sampling Site Berlin:

Laboratory	Lead	Cadmium	Arsenic	Nickel
A (AAS)				
B (AAS)		1	2	
C (AAS)				
D (AAS)		2		
B (ICP-MS)		1		
D (ICP-MS)		1		

### Number of Outliers, Sampling Site Antwerp:

Laboratory	Lead	Cadmium	Arsenic	Nickel
A (AAS)				1
B (AAS)	3	1		
C (AAS)	2	1	1	
D (AAS)	1			1
B (ICP-MS)				
D (ICP-MS)				2

## Annex D: Comparison GF-AAS vs. ICP-MS

Diagram D1: Lead at the sampling site Madrid

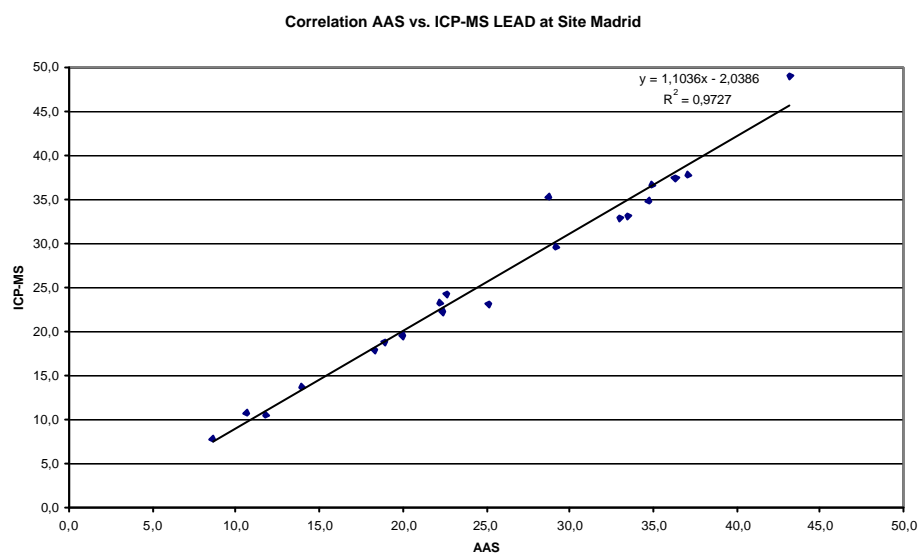


Diagram D2: Lead at the sampling site Bristol

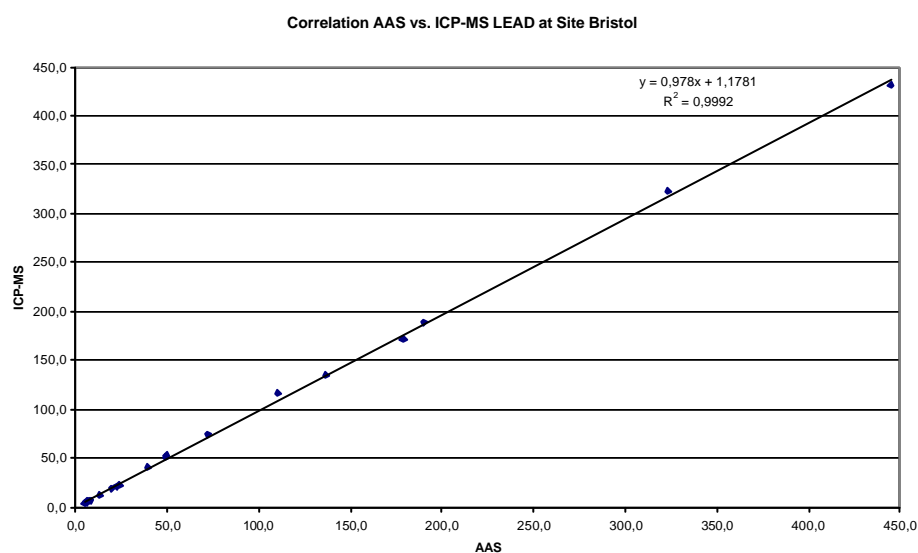


Diagram D3: Lead at the sampling site Berlin

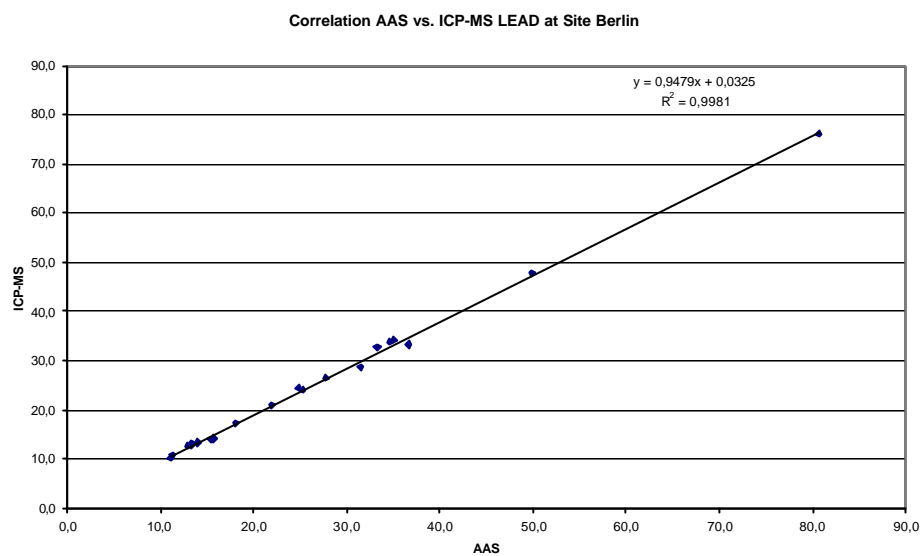


Diagram D4: Lead at the sampling site Antwerp

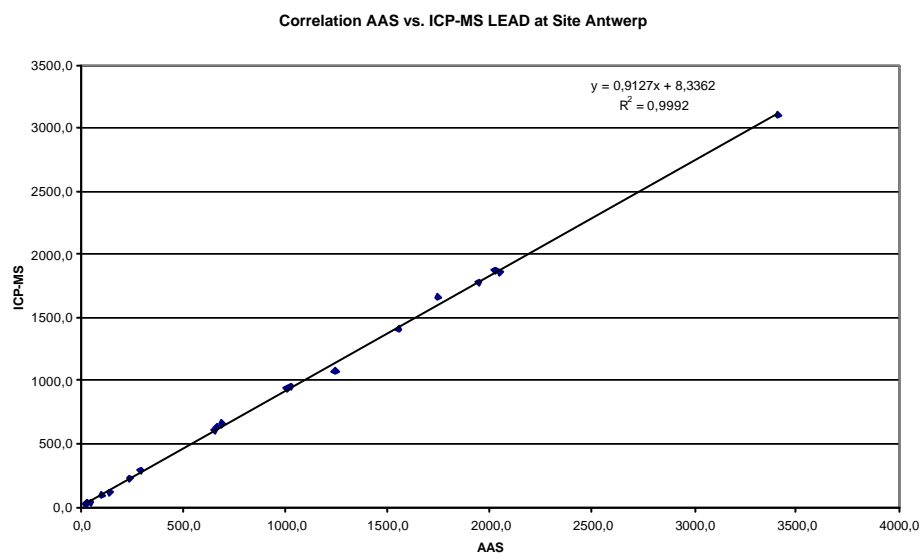


Diagram D5: Cadmium at the sampling site Madrid

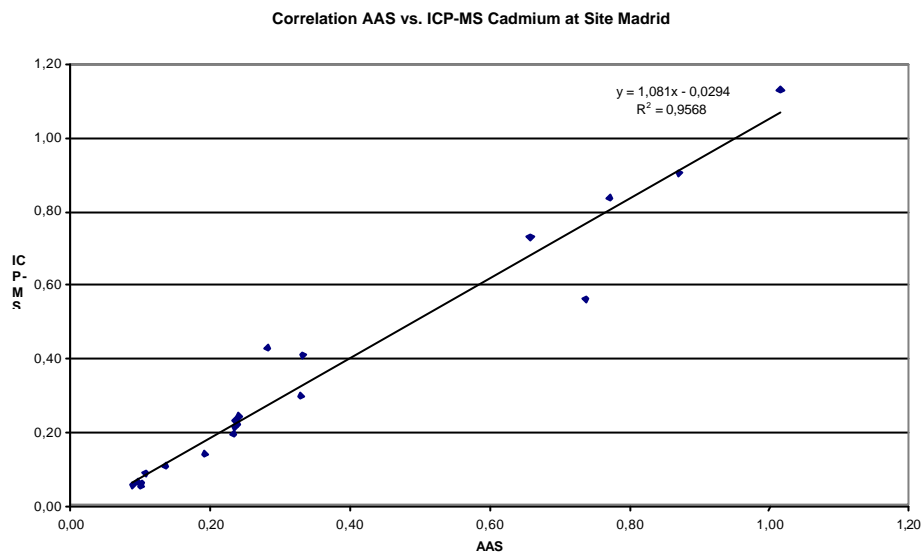


Diagram D6: Cadmium at the sampling site Bristol

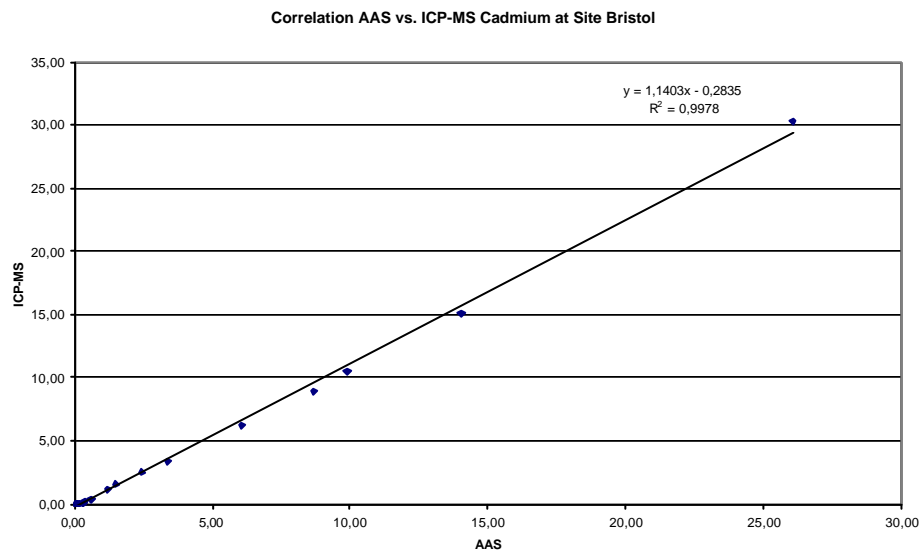


Diagram D7: Cadmium at the sampling site Berlin

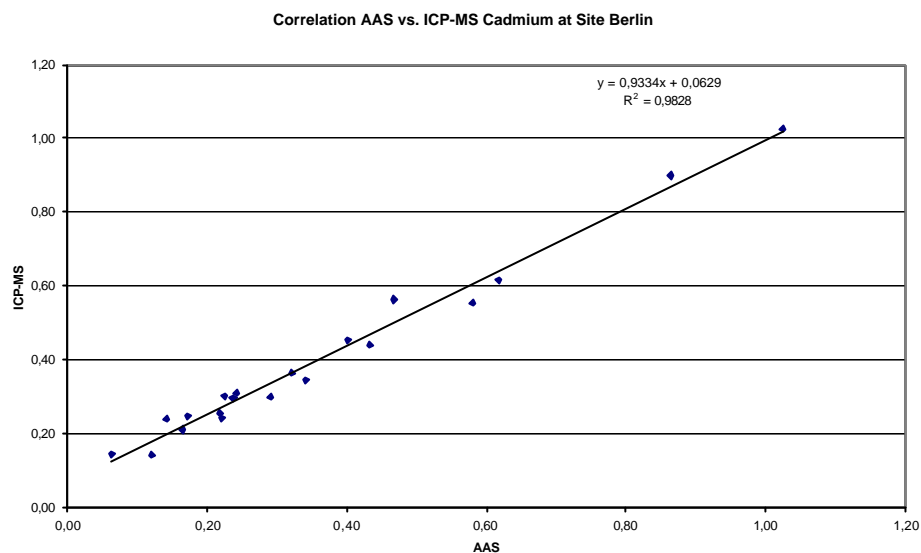


Diagram D8: Cadmium at the sampling site Antwerp

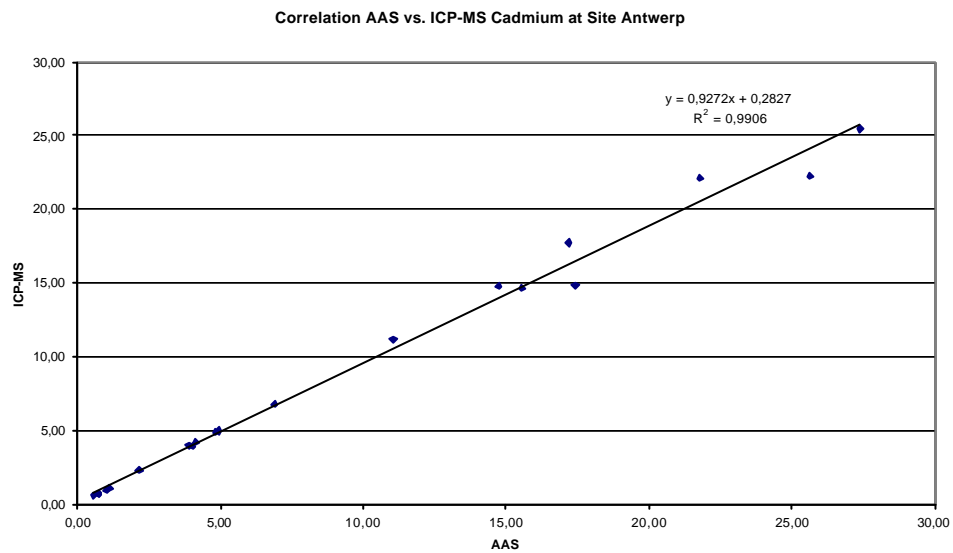


Diagram D9: Arsenic at the sampling site Madrid

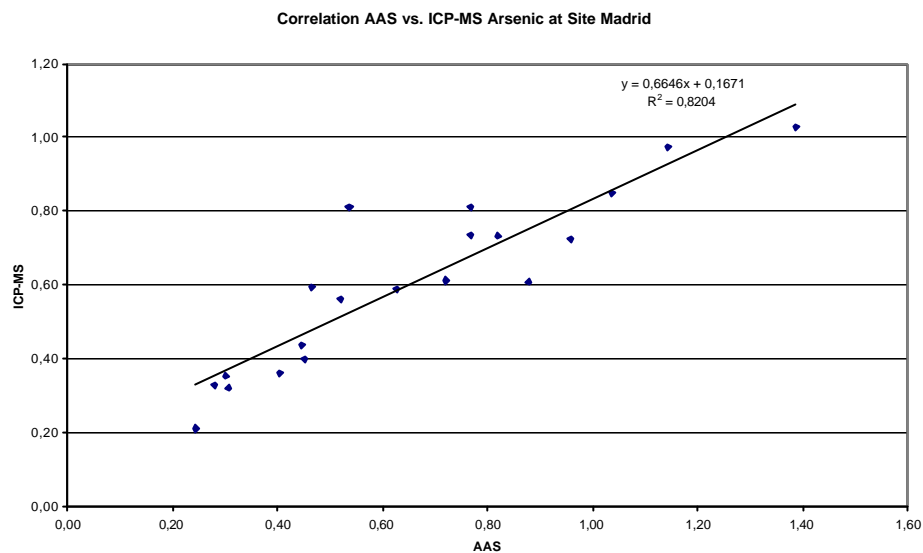


Diagram D10: Arsenic at the sampling site Bristol

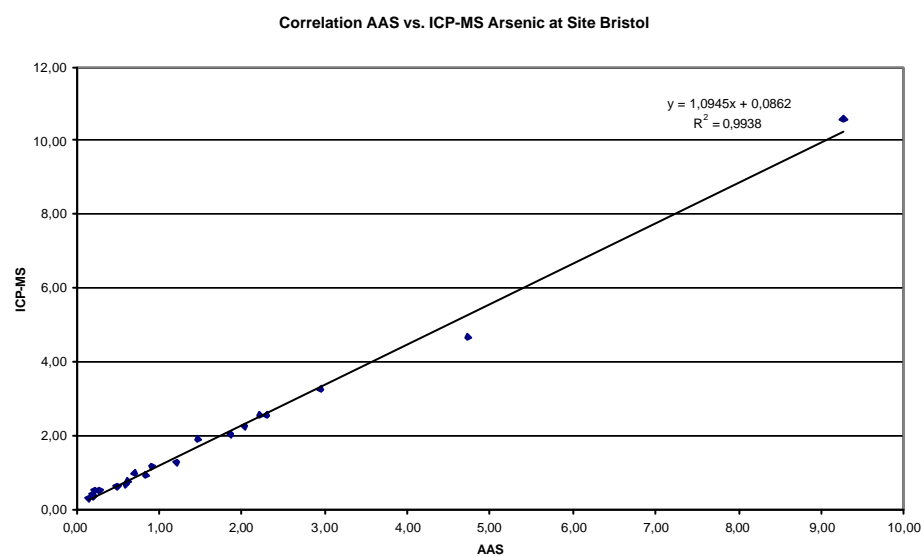


Diagram D11: Arsenic at the sampling site Berlin

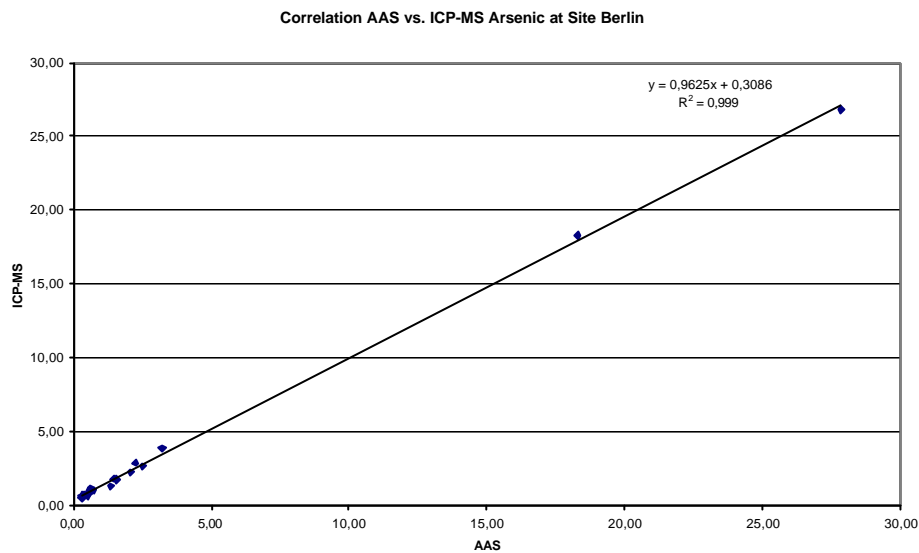


Diagram D12: Arsenic at the sampling site Antwerp

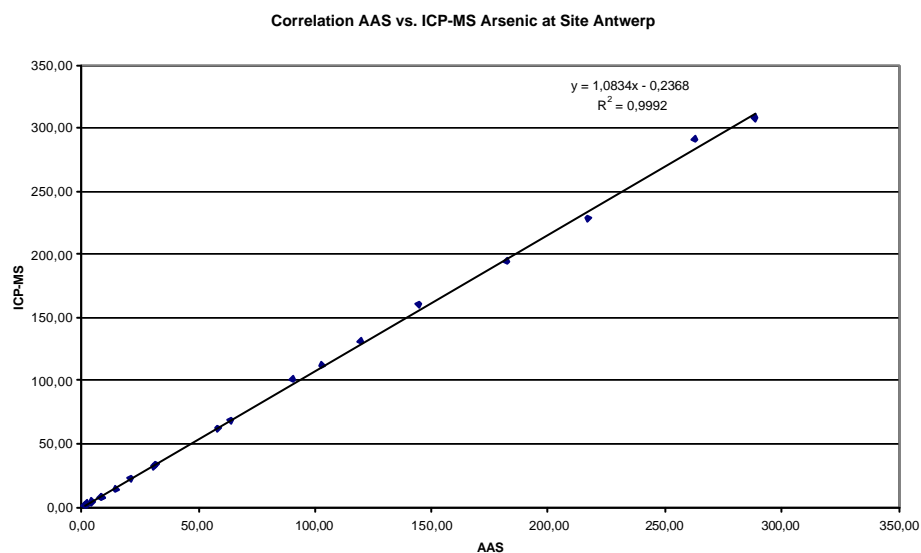




Diagram D13: Nickel at the sampling site Madrid

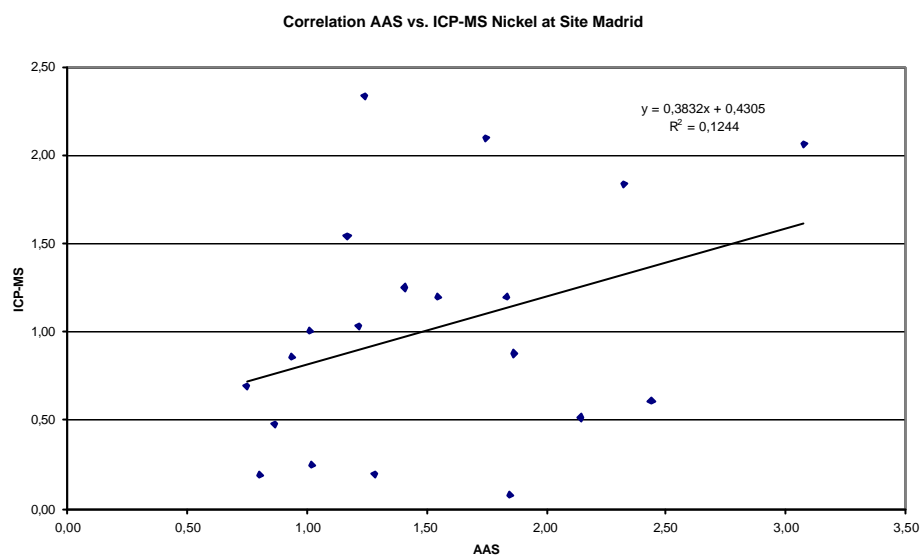


Diagram D14: Nickel at the sampling site Bristol

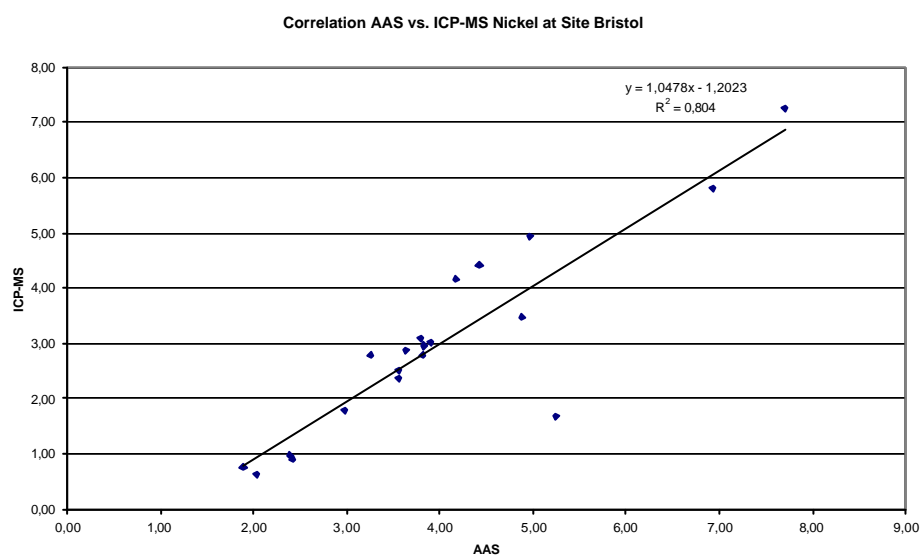


Diagram D15: Nickel at the sampling site Berlin

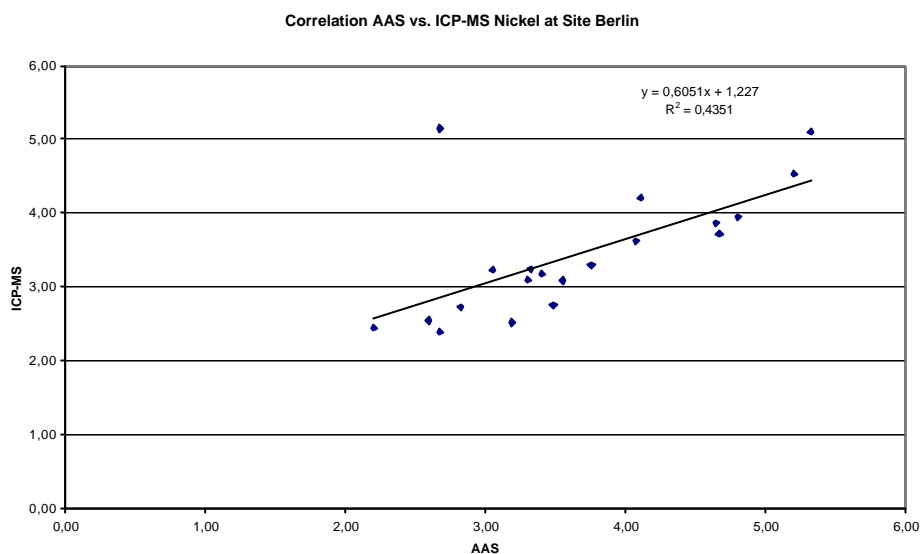
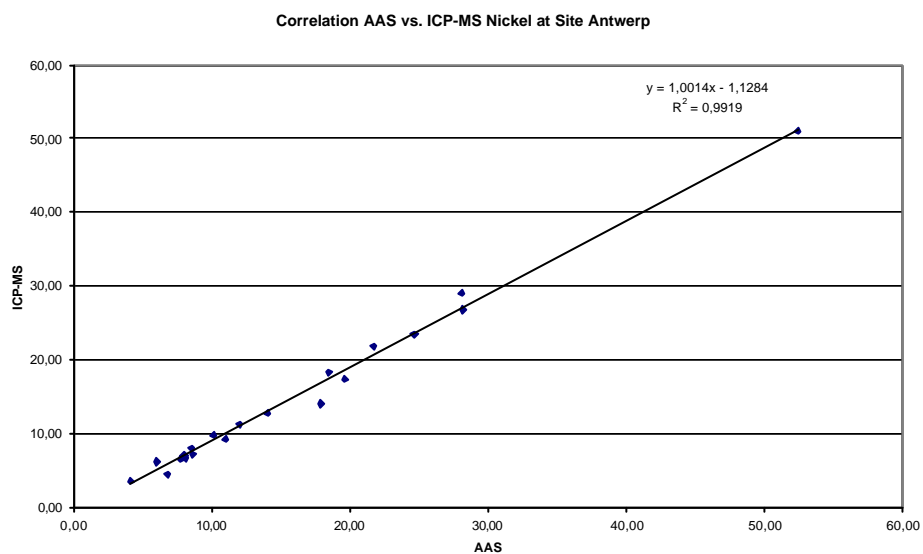


Diagram D16: Nickel at the sampling site Antwerp



## Annex E: Comparison Quartz vs. Membrane filters (AAS technique)

Diagram E1: Lead with AAS Quartz and Membrane filters at the site Antwerp

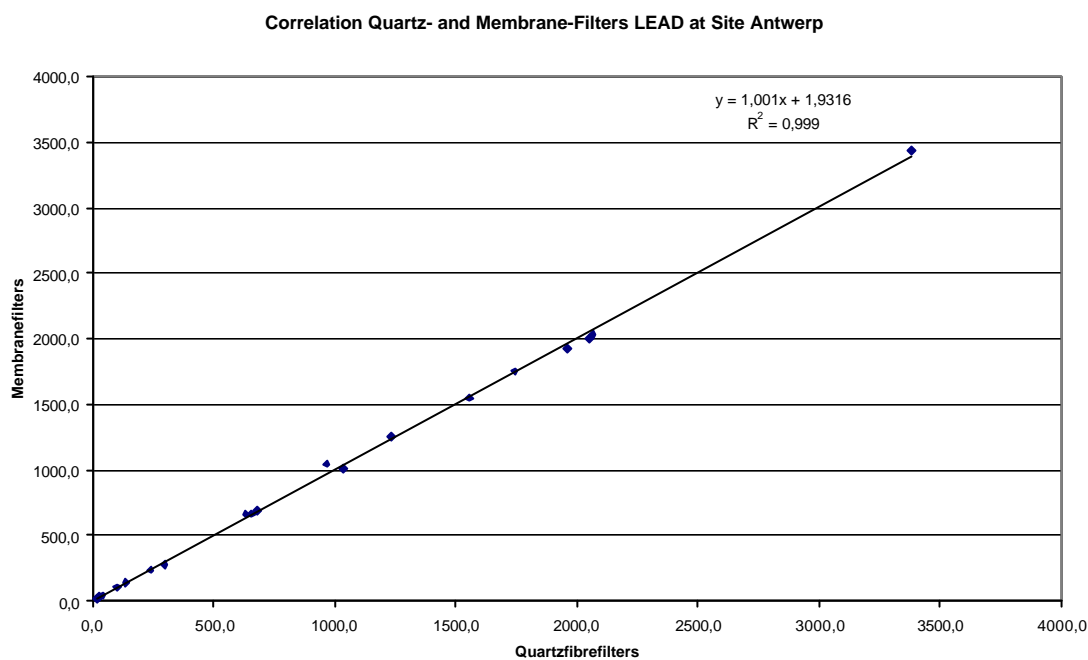


Diagram E2: Cadmium with Quartz and Membrane filters at the site Antwerp

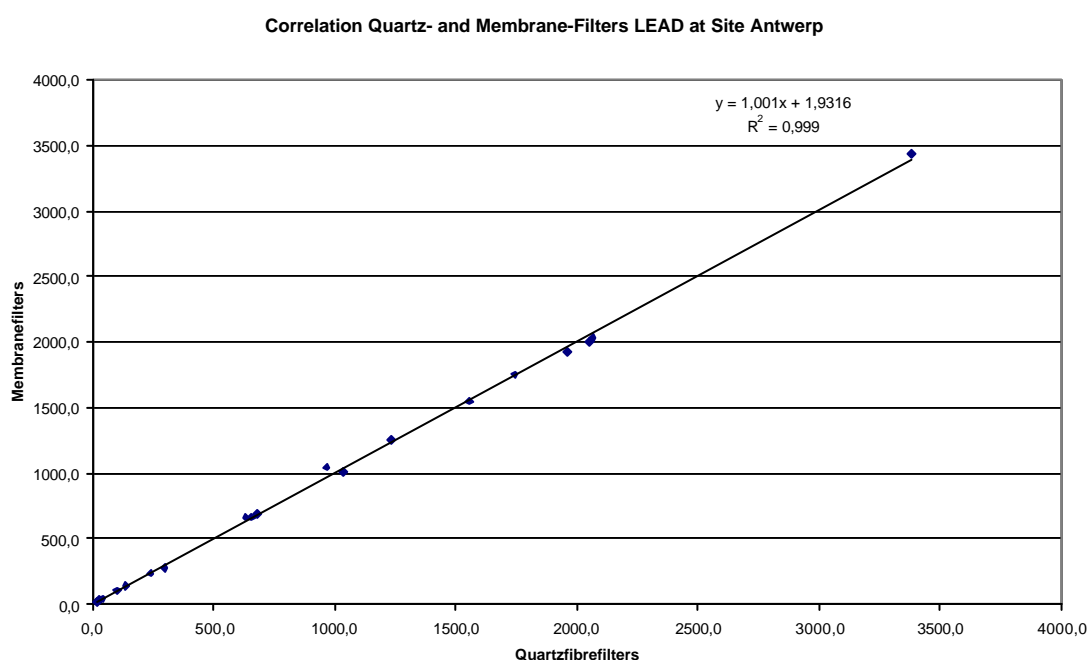


Diagram E3: Nickel at the sampling site Berlin

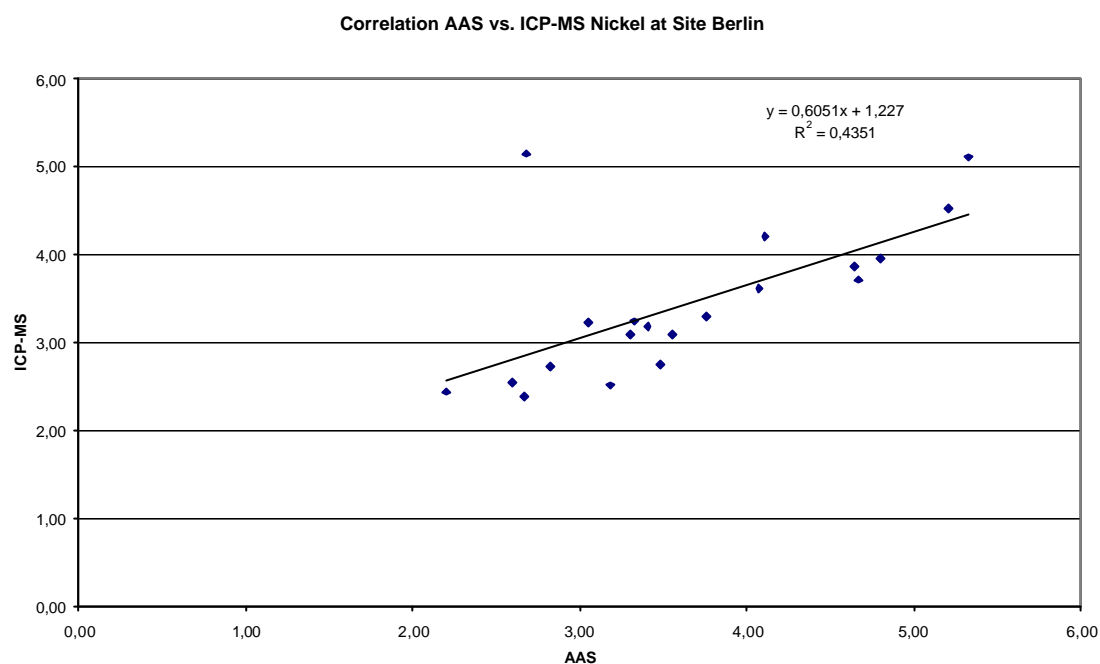


Diagram E4: Nickel at the sampling site Antwerp

