Final Report WG 14 Part C Field Tests Madrid

Instituto de Salud Carlos III

Ministerio de Sanidad y Consumo
Centro Nacional de Sanidad Ambiental

Area de Contaminación Atmosférica

GENERAL REPORT FOR CEN / TC 264 WG 14 OF THE MADRID FIELD WORK

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REPORT OF LAB A

Ministerio de Sanidad y Consumo
Centro Nacional de Sanidad Ambiental
Área de Contaminación Atmosférica

"REFERENCE METHOD FOR THE DETERMINATION OF Pb, Cd, As AND Ni IN AMBIENT AIR"

MINIMUM VALIDATION PROGRAMME
CEN/ TC 264 WG 14
FIELD TEST – MADRID

INSTITUTO DE SALUD CARLOS III

ÁREA DE CONTAMINACIÓN ATMOSFÉRICA

1 Background

This report is made by the Instituto de Salud Carlos III (ISC III), as response to a call by the CEN/TC 264 /WG 14 for the preparation of the field test, which is part of the minimum validation programme (MPV). The MPV is funded by the DG XI of the European Commission.

2 AIM

In the report the results obtained of the analysis of 40 Muntkell filters used by 2 LVS-3D PM10 samplers (SP-01 and SP-02) during a sampling period of approximately 24 hours, between the 4th of May and the 25th of May are include, performed in the ISC III owned Madrid Field Station. The analytical work was performed according the method set on documents CEN/TC 264/WG 14 N 140 rev3 and CEN/TC 264/WG 14 N 245.

Instituto de Salud Carlos III atmospheric pollution station at Madrid.

3 MATERIALS

3.1 Filter material

Quartz fibre filter Munktell MK 360 (50 mm). The filter material was delivery by UBA / Austria.

3.2 Reagents

Nitric acid (65 % HNO_3), suprapure Merck art n 100 441
Hydrogen peroxide 30 %, H_2O_2, pro analysis, Merck art n 107 209
Pure water, H_2O, Milli Q (< 0,1mS/m)

3.3 Reference materials

NIST 1648 Urban Particulate matter
NIES N 8 Vehicle Exhaust particulate matter

To determine the recovery rates the digestions were carried out without filters.

4 ANALYTICAL METHOD

4.1 Samples Digestion

Apparatus:

- Anton Paar Multiwave, microwave system with IR temperature sensor, unpulsed power setting, was used for sampling digestion.

- **Digestion matrix**

8 ml HNO_3 + 2 ml H_2O_2
Dilution Volume: 50 ml

- **Digestion vessels**

Quartz high pressure vessels HQ 50 with a 50 ml volume.

- **Precleaning steps for glassware**

It was carried out according the procedure described in document CEN/TC 264/WG 14 N 245.

- **Digestion procedure**

Microwave programme for a power controlled device (6 vessels with 50 ml each)

Step 1 – 20 minutes – 100-1000 W
Step 2 – 15 minutes – 800 W
Step 3 – 15 minutes – cooling by air ventilation

After process step 3, the vessels were opened and the contents were transferred into calibrated 50 ml quartz flasks and diluted to 50 ml with pure water.

4.2 Analytical conditions

The measurements were made using an Atomic Absorption Spectrometer Perkin Elmer mod Aanalyst-100 with a graphite furnace Perkin Elmer HGA – 800 and autosampler AS-72, with deuterium as background correction. Pyrocoated graphite tubes with platform were used for the atomisation.

The analytical conditions were performed according Document CEN/TC 264/ WG 14 N 245.

5 RESULTS OF FIELD TESTS

The results are in an excel file, called ANNEX_WG14_MadridFW_lab A.xls.

6 DISCUSSION

Also, as a voluntary basis the filters were reanalysed for Cadmium changing the mineralisation temperature, according the ISC III procedure to heavy metal rain analysis. Therefore 250 ºC mineralisation and 1 700 ºC atomisation temperatures were used. Clearly, the results showing on the following tables demonstrated a better method sensibility for low concentrations.

Cd ng/m3	Lab A		Lab B		Lab C		Lab D		Lab D-ICP	
Day	SP-01	SP01 ISC III	SP-08	SP-10	SP-05	SP-07	SP-03	SP-04	SP-03	SP-04
4-5-01	0,09	0,19	0,08	0,16	0,25	0,18	0,12	0,13	0,13	0,15
5-5-01	n.d.	0,09	0,15	0,10	0,09	0,10	0,05	0,06	0,07	0,08
6-5-01	0,07	0,15	0,07	0,16	0,10	0,12	0,08	0,09	0,09	0,10
7-5-01	0,23	0,38	0,22	0,28	0,26	0,27	0,21	0,29	0,25	0,31
8-5-01	0,20	0,34	0,23	0,28	0,26	0,29	0,21	0,22	0,23	0,24
10-5-01	0,19	0,29	0,30	0,87	0,28	0,28	0,22	0,22	0,21	0,28
12-5-01	0,11	0,11	0,20	0,24	0,26	0,33	0,16	0,16	0,18	0,18
13-5-01	0,05	0,05	0,12	0,13	0,15	0,14	0,09	0,11	0,09	0,13
14-5-01	0,89	0,90	0,74	0,30	1,00	0,93	0,93	0,16	0,95	0,20
15-5-01	0,12	0,17	0,22	3,86	0,21	0,20	0,18	0,93	0,22	1,00
16-5-01	0,86	0,85	0,72	0,72	0,98	1,00	0,91	0,89	0,98	0,94
17-5-01	0,74	0,73	0,67	0,69	0,85	0,84	0,80	0,88	0,89	0,93
18-5-01	0,03	0,07	0,14	0,16	0,14	0,13	0,09	0,10	0,13	0,13
19-5-01	0,05	0,12	0,12	0,15	0,13	0,11	0,08	0,08	0,10	0,11
20-5-01	0,26	0,33	0,33	0,35	0,39	0,38	0,31	0,34	0,34	0,34
21-5-01	1,00	1,00	0,84	0,81	1,15	1,15	1,12	1,18	1,19	1,25
22-5-01	0,58	0,62	0,58	0,60	0,74	0,68	0,64	0,84	0,68	1,04
23-5-01	0,17	0,22	0,39	0,26	0,24	0,27	0,22	0,21		0,25
24-5-01	0,29	0,31	0,24	0,41	0,43	0,41	0,38	0,37	0,48	0,37
25-5-01	0,24	0,28	0,33	0,24	0,27	0,29	0,21	0,21	0,30	0,22

Comparison results of Cd (ng/m^3) using the ISC III method for sampler number 1.

Cd ng/m3	Lab A		Lab B		Lab C		Lab D		Lab D-ICP	
Day	SP-02	SP-02 ISCIII	SP-08	SP-10	SP-05	SP-07	SP-03	SP-04	SP-03	SP-04
4-5-01	0,08	0,19	0,08	0,16	0,25	0,18	0,12	0,13	0,13	0,15
5-5-01	0,01	0,11	0,15	0,10	0,09	0,10	0,05	0,06	0,07	0,08
6-5-01	0,02	0,15	0,07	0,16	0,10	0,12	0,08	0,09	0,09	0,10
7-5-01	0,15	0,29	0,22	0,28	0,26	0,27	0,21	0,29	0,25	0,31
8-5-01	0,18	0,35	0,23	0,28	0,26	0,29	0,21	0,22	0,23	0,24
10-5-01	0,16	0,22	0,30	0,87	0,28	0,28	0,22	0,22	0,21	0,28
12-5-01	0,08	0,15	0,20	0,24	0,26	0,33	0,16	0,16	0,18	0,18
13-5-01	0,03	0,05	0,12	0,13	0,15	0,14	0,09	0,11	0,09	0,13
14-5-01	0,94	0,91	0,74	0,30	1,00	0,93	0,93	0,16	0,95	0,20
15-5-01	0,11	0,13	0,22	3,86	0,21	0,20	0,18	0,93	0,22	1,00
16-5-01	0,89	0,89	0,72	0,72	0,98	1,00	0,91	0,89	0,98	0,94
17-5-01	0,71	0,74	0,67	0,69	0,85	0,84	0,80	0,88	0,89	0,93
18-5-01	0,07	0,07	0,14	0,16	0,14	0,13	0,09	0,10	0,13	0,13
19-5-01	0,06	0,11	0,12	0,15	0,13	0,11	0,08	0,08	0,10	0,11
20-5-01	0,28	0,30	0,33	0,35	0,39	0,38	0,31	0,34	0,34	0,34
21-5-01	0,87	0,89	0,84	0,81	1,15	1,15	1,12	1,18	1,19	1,25
22-5-01	0,60	0,64	0,58	0,60	0,74	0,68	0,64	0,84	0,68	1,04

23-5-01	0,17	0,23	0,39	0,26	0,24	0,27	0,22	0,21		0,25
24-5-01	0,14	0,20	0,24	0,41	0,43	0,41	0,38	0,37	0,48	0,37
25-5-01	0,10	0,17	0,33	0,24	0,27	0,29	0,21	0,21	0,30	0,22

Comparison results of Cd (ng/m^3) using the ISC III method for sampler number 2.

REPORT OF LAB B

Stanger

Science and Environment

DRAFT Report

CEN TC264/WG14 Minimum Validation Programme: Field Tests – Madrid. UK Report

15 September 2001

DRAFT Report

CEN TC264/WG14 Minimum Validation Programme: Field Tests – Madrid. UK Report

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Background

This report is made by the UK Consortium (comprising Stanger Science and Environment, CRE Group Ltd and Harwell Scientifics Ltd) for the Minimum Validation Programme (MVP) of CEN TC264/WG14. The MVP is funded in the UK jointly between the UK Department for Environment, Food and Rural Affairs (formerly the Department of the Environment, Transport and the Regions) and DG XI of the European Commission.

Aim / Overview

The MVP comprises separate components, which include a laboratory test, the preparation for the field tests and the preliminary field tests and the field tests. A detailed overview of the MVP is provided in CEN/TC 264/WG14 N95 – Description of the Minimum Validation Programme. Additional documents provide details with respect to the preparation of the Field Tests (CEN/TC 264/WG14 N147 and PTN09) and the execution of the Preliminary Field Tests and Field Tests (CEN/TC 264/WG14 N140Rev5).

This report concerns the analysis of filters provided through the sampling of fine particulates (PM_{10}) at the field site in Madrid. The purpose of the Field Tests is to perform 'field' validation of the draft standard for Cd, As and Ni currently being considered by CEN for the implementation of the Fourth Daughter Directive by the EU for the setting of Limit Values for these pollutants.

The Field Tests will be carried out at four measurement sites (2 industrial and 2 urban). Laboratories from four Member States currently participate in the MVP. At the measurement site, PM_{10} samplers (10 of), are run in parallel for the purposes of carrying out duplicate measurements of metal concentrations by each laboratory. Sampling is undertaken by each participating Member State in turn. Having completed the sampling for a period of four weeks (20 days of 24-hour samples) the laboratory responsible for the sampling distributes the samples amongst the other laboratories for analysis. Laboratories report results back to the sampling host participant responsible for the collation of all data. Two laboratories analyse cellulose acetate filters whilst the other two analyse quartz fibre filters.

Specific to the UK analysis, ICP-MS is included (initially as a voluntary component) in addition to GF-AAS analysis funded by the European Commission. The purpose of this inclusion is to seek equivalence of a former 12-month monitoring exercise carried out within the UK with the proposed reference method for ambient metals. This is subject to a separate UK specific report and is will not be considered further here.

Objectives

- To determine the performance characteristics of the proposed reference method in its entirety (e.g. quantification limits, repeatability and

reproducibility for Pb, Cd, As andNi) samples in accordance with EN 12341 with a Low Volume Sampler.
- To estimate the uncertainty budgets of the sampling step and the expanded uncertainty of the complete method.

Materials

Filter material:

The filter media were as supplied by UBA/Austria i.e. Sartorius Cellulose acetate 3µm (50mm) membrane filters.

Reagents:

Nitric acid (Primar grade from Fisher Scientific)
Hydrogen peroxide
Pure water (18mΩ, <0.1 mS/m)

Reference materials:

NIST 1648 (10mg used for QA/QC steps). For the determination of recovery rates, filters were not included in the analytical step.

NIES No.8 (80mg used for QA/QC steps). For the determination of recovery rates, filters were not included in the analytical step.

Digestion procedure

Using 100ml XP1500 vessels. The digestion matrix was 8ml concentrated nitric acid + 2ml hydrogen peroxide.

The digestion program was as follows;

Step	Ramp time	Temp	Hold time	Power Pressure
1	20mins	220°C	25 min.	1200W max 800psi
2	cooling by air ventilation		20 min.	0W

A typical trace from the temperature and pressure sensors is shown in Appendix 1.

After cooling the contents of the vessels were transferred to 50ml volumetric flasks and made up to volume with pure water.

ICP-MS analysis

Standards: Single element 1000 µg/ml certified standard solutions were obtained from Glen Spectra.

Calibration standards were prepared at 0.1, 0.5, 1.0, 10, 25, 100, and 250 (in the case of lead only) µg/l by the following procedure.

A 10 µg/ml multi-element stock solution was prepared by dilution of appropriate aliquots of single element certified standard solutions. A secondary multi-element stock solution was prepared at 100 µg/l by dilution of 1ml of the 1000 µg/ml standard to 100ml using 16% nitric acid.

An internal standard stock solution was prepared at 10 µg/ml by dilution of appropriate aliquots of the single element certified standard solutions using 16% nitric acid. This solution contained germanium, yttrium, indium and bismuth.

The calibration standards were prepared by diluting appropriate volumes of the secondary multi-element stock solution and 400µl of the internal standard stock solution to 100 ml with 16% nitric acid.

Operating conditions of the ICP-MS

RF Generator	1350W
Plasma gas flow	13.5 l/min
Auxillary gas flow	0.8 l/min
Nebuliser gas flow	0.95 l/min
Dwell time	40ms
Sweeps	50

Internal standards (all at 40 µg/l)

72 Germanium
89 Yttrium
115 Indium
209 Bismuth

All masses were monitored for the metals of interest. The data reported was for masses Ni 60, Cd 111, As 75, Pb 208.

GF-AAS analysis

{Details to follow}

Results

Analysis was carried out using ICP-MS and GF-AAS anaysis. For ICP-MS, analysis was carried out by CRE Group Ltd whilst for GF-AAS analysis was undertaken by Harwell Scientifics Ltd. Fort the purposes of this draft report all elements with the exception of arsenic (As) are reported.

Recovery Rates

Table 6.1 summarises the results of the recovery rates for both ICP-MS and GF-AAS (where available). In general, recovery rates were good.

For ICP-MS analysis recovery rates for all metals were generally within the margins of tolerance with the exception of Pb for NIST where only 95.7% recovery was obtained and the reported concentration was 6269 mg/kg. For NIES, over-recovery of As was found (113.4%) resulting in a reported concentrations of 2.9 mg/kg.

For GF-AAS low recovery for Cd was observed. The recovery was only 85% resulting in a reported concentration of 64 mg/kg against a certified value of 75 mg/kg. A similar recovery rate for Cd was found for the NIES standard (82%) also resulting in a reported concentrations outside the margins of tolerance, albeit only just.

Period Mean Concentrations

Table 6.2 summarise the period mean concentrations (ng/m^3) obtained across the two samplers (SP8 and SP9/10) undertaking analysis of samples using ICP-MS and GF-AAS as determined from daily measurements shown in Appendix 2.

Results show low variable levels of pollutant concentrations on a day-by-day basis (Appendix 2). For the period mean concentrations determined over the period of sampling as summarised above, good agreement is shown between the two analytical methods, although much lower concentrations of Cd and As are recorded at the site in Madrid when compared to the concentrations of Pb and Ni. Results for As determined through GF-AAS are not yet available and will be provided accordingly.

Table 1 Summary of Recovery Rates determined for NIST and NIES Certified Reference Material using ICP-MS and GF-AAS analyses.

Determinant (CRM Value)	ICP-MS		GF-AAS	
	Value (mg/kg)	% Recovery	Value (mg/kg)	% Recovery
NIST				
Pb: 6550 ± 80 mg/kg	6269	95.7	6690	102.1
Cd: 75 ± 7 mg/kg	76.4	101.9	64.1	85.5
As: 115 ± 10 mg/kg	119.1	103.6		
Ni: 82 ± 3 mg/kg	85.9	104.8	75.9	92.6
NIES				
Pb: 219 ± 9 mg/kg	225	102.9	242	110.6
Cd: 1.1 ± 0.1 mg/kg	1.1	102.2	0.9	82.2
As: 2.6 ± 0.2 mg/kg	2.9	113.4		
Ni: 18.5 ± 1.5 mg/kg	18.0	97.5	18.2	98.3

Table 2 Summary of Period Mean Pb, Cd, Ni and As concentrations (ng/m^3) across samplers using membrane filters at the Madrid site.

Determinant	SP8		SP9/10	
	ICP-MS	GF-AAS	ICP-MS	GF-AAS
Pb	27.73	25.59	29.78	26.06
Cd	0.406	0.336	0.624	0.537
As	0.691		0.662	
Ni	2.181	2.098	2.192	1.995

Results of field tests

The results are for samplers numbers 8 and 9 in excel files, called

ANNEX_WG14_MadridFW_labB.xls
ANNEX_WG14_MadridFW_lab B ICP.xls

Conclusions

Results of the analysis show day to day variation in ambient concentrations of each of the pollutants concerned. For Cd, low recovery using GF-AAS was found when compared to the recovery of other metals using GF-AAS.

Initial comparisons between the samplers indicate good agreement between the two units both on a day-to-day determination of concentrations and also for period mean statistics.

Appendix 1. Temperature (^{o}C) and Pressure profile (psi) during microwave digestion.

REPORT OF LAB C

MINIMUM VALIDATION PROGRAMME
CEN TC264/WG14 –PART 3/3
FIELD TESTS - MADRID
JULY 2001

VMM-report

Department Networks and Research
Air Quality Networks - Heavy Metals
Elke Adriaenssens - Natacha Claeys

According the document:
CEN/TC264/ WG14 N095 - Description of the Minimum Validation Program(MVP)

And additional documents:
CEN/TC264/WG 14 N147 and PTN009 – Preparation of Field Tests
CEN/TC264/WG 14 N140rev5 – Proposal for preliminary tests and field tests

1 Background

This report is made by the participant VMM (Belgium) for the Minimum Validation Programme (MVP) of CEN/TC264/WG 14. The MVP is funded by DG XI of the European Commission.

2 Aim/Overview

A laboratory test, the preparation of field tests and the preliminary field tests are performed according the MVP. Within these tests the suitability of the filter types and the analytical procedures and the sampling procedure to be described in the proposed reference method has been proven.

The purpose of the field tests is to perform the „**field**“ validation of the draft standard. The field validation includes all steps of the draft standard including sampling, sample preparation and analysis of the samples.
The field validation tests will be carried out at four measurement sites (2 industrial and 2 urban). Four labs will participate in the tests. At the measurement site 10 PM10 samplers will run in parallel. For carrying out duplicate determinations each lab will analyse two

PM10 samplers. All sampling will be carried out with the same type of LVS-PM10 sampler and at each measurement site; one lab will be responsible for operating all samplers and also for delivering the exposed filters to the other participating labs. The sampling period will be four weeks with 20 days of 24 hours sampling. Two labs will use quartz fibre filters, the two other labs use cellulose acetate filters for the field tests.

3 Objectives

- To determine the performance characteristics of the complete method, e.g. quantification limits, repeatability and reproducibility for Pb, Cd, As and Ni sampled according to EN 12341 with a LVS device.
- To estimate the uncertainty budgets of the sampling step (as far as possible) and the expanded uncertainty of the complete method.

4 Materials

Filter material: (The filter materials are delivered by UBA/Austria)
VMM lab (Lab C) membrane filter Sartorius Cellulose-acetate 3µm (50mm)

Real filters + field filter blanks: (The filters are delivered by Spain, Instituto de Carlos)
VMM lab (lab C) received 40 real filters (20 filters from sampler 05 and 20 filters from sampler 07) and 4 field filter blanks from the field test at Spain.

Reagents:
nitric acid 70-71 %, HNO3,Baker INSTRA ANALYZED Suprapure nr 9598-0500
hydrogen peroxide 30 %, H2O2, pro analysis, Merck art.no.: 107209
Ultrapure water, H2O, MILLIQ PLUS , (18,2 Mcm, < 0,1 mS/m)

Reference materials:
NIST 1648 Urban Particulate Matter
NIES No.8 Vehicle Exhaust Particulate Matter

4 Results

4.1. Digestion procedure

There were no changes made at the digestion procedure. The detailed procedure is described in document CEN/TC264/WG14/N199.
Five digestion runs were carried out. The digestion series 1 to 4 consisted of 1 reagent blank, 1 lab filter blank, 1 field filter blank, 1 NIST standard, 1 NIES standard and 7 real filters. In the 5th run only real filters were digested.

4.2. Analytical results

The analysis was done with GF-AAS. Cd and Pb were analysed together. In the previous analyses also Ni and As were measured together. At the moment a lowering background for arsenic is detected in function of time. For this reason, the nickel and arsenic analyses were splitted and both elements were measured in a mono element analysis. This gave much better results for arsenic. The detailed analytical conditions are described in document CEN/TC264/WG14/N199.

The 40 real filters were measured. After every 10th real filter a reagent blank, a lab filter blank, a field filter blank, a NIES and NIST reference material and a quality control standard were measured. The results are presented in the Excel file lab_C_madrid.xls. The VMM received 4 field filter blanks from the Instituto de Carlos. From every sampler 2 field filter blanks were taken on the following dates:

04/05/04
25/05/01

For arsenic, the different blank analyses are below the detection limit. For Cd, the blank values are below or around the detection limit. The concentration of the blank samples are generally below the detection limit for Pb, only one time a relatively high (1.1 ppb) concentration is measured. For nickel, the reagent and lab filter blank concentrations are mostly below the detection limit. For the field filter blanks concentrations of circa 1 ppb are measured.

Analysing the NIST and NIES reference materials give very good results for Pb (98.3 – 100.6% recovery). For Cd the NIES reference material results in a recovery of 99.1%, although a relatively high deviation is observed (9%). Measuring the NIST reference material results in a recovery of 93.7% for Cd. For the nickel analyses, the same tendencies as observed for Cd, are found. NIES gives a recovery of 100.6%, NIST of 91.5%. For As good results are obtained for both the reference materials, a recovery of 102.2% for NIST and 111.8 % for NIES is obtained.

5 RESULTS

The results is in an excel file, called ANNEX_WG14_MadridFW_lab C.xls

REPORT OF LAB D

Reference Method for the Determination of

Pb, Cd, As and Ni in Ambient Air

Minimum Validation Programme

Field Test Madrid

(MVP WG 14)

Spittelauer Lände 5, A-1090 Wien

1. BACKGROUND

This report is made by the participant Lab D (UBA Austria) for the field test Madrid which is part of the Minimum Validation Programme (MVP) of the Reference Method for the Determination of Pb, Cd, As and Ni in Ambient Air (in response to a call by CEN/TC 264/WG 14):
The MVP is funded by DG XI of the European Commission.

2 AIM

The purpose of the field tests is to show the suitability of the reference methode for the determination of Pb, Cd, As and Ni in ambient air.
At 4 sites (Madrid,Bristol,Antwerp and Berlin) the ambient air is sampled on filters which are then digested and analysed.

3 OBJECTIVES

The UBA performed the analysis of the field test according to the guidlines of N 140rev4.
The UBA lab analysed quartz fibre filters, Munktell MK 360 (diameter: 50mm).
This field test includes:

- Check of recovery rates of CRM´s (NIST 1648, NIES No.8)
- Check of reagent blanks, filter blanks and field filter blanks
- Analysis of the the filters, sampled in Madrid

Materials and equipment

Filter material: quartz fibre filters Munktell MK 360 50mm diameter

Real filters: (The filters are delivered by Spain, Instituto de Carlos)
UBA recieved 40 real filters and 4 field filter blanks

Reagents:
nitric acid 65 %, HNO_3, suprapure (1 l = 1,4 kg), Merck art.no.: 100441
hydrogen peroxide 30 %, H_2O_2, pro analysis, Merck art.no.: 107209
pure water, H_2O, MILLIQ^{PLUS}, (18,2 MΩcm, < 0,01 mS/m)

4. DIGESTION PROCEDURE:

4.1 Precleaning steps for glassware

All digestion vessels were prerinsed with water and cleaned by leaching with hot nitric acid (~5 ml) in the microwave unit.

microwave precleaning vessel programme:

step 1	5 min.	500-1000 W
step 2	5 min.	1000 W
step 3	15 min.	cooling by air ventilation

After process step 3 the contents of the vessels were disposed. The vessels were washed with pure water (three times) and dried before use. All volumetric quartz flasks and funnels were acid washed and rinsed with pure water.

4.2 Digestion conditions

4.2.1 Apparatus

A Anton Paar/Perkin Elmer MULTIWAVE B30MC05A microwave system with unpulsed power setting was used for digestion of filters. The programme is listed below.

Microwave programme:

step 1	20 min.	100-1000 W
step 2	15 min.	800 W
step 3	15 min.	cooling by air ventilation

Digestion mixture: 8 ml HNO_3 + 2 ml H_2O_2 (for filter diameter 50 mm)

Digestion vessels: 50 ml quartz-high-pressure vessels (HQ 50 – pressure limit: 75 bar)

4.2.2 Description of digestion steps

In **step 1**, the heating-phase, the microwave increases the power from 100 to 1000 W. During this period temperature in the vessels climbs from room-temperature to approximately 180°C. The pressure in the vessels also increases from the start pressure (depending of the contents, in this case about 6 bar) to about 45 bar.

In **step 2** according to the programme the power is constant at 800 W. (If the pressure limit of 72 bar is reached, the microwave system reduces power continuously. The power will be stopped completely, if the pressure exceeds 75 bar.). The temperature climbs from 180 to 220°C (+/- 10°C).

In **step 3** the microwave reduces the power to 0 W and the vessels are cooled by air ventilation, so at the end of the programme the pressure is down to about 10 bar and the temperature about 60°C.

After end of step 3 the vessels are opened and the contents are transferred into calibrated 50 ml quartz flasks and diluted to 50 ml with pure water.

5 ANALYTICAL CONDITIONS

All measurements according to the requirements of MVP WG 14 were performed using a simultan graphite furnace atomic absorption spectrometer SIMAA 6000, Perkin Elmer, with transverse heated graphite atomizer (THGA). Pyrocoated graphite tubes with End Caps are used for formation of atoms.

5.1 Cadmium, Lead – GF-AAS

lamps:	electrodeless discharge lamps (EDL)			
wavelength:	Pb	283,3 nm	Cd	228,8 nm
current:	Pb	450 mA	Cd	240 mA
gas:	Argon			
background correction:	Zeeman			
sample volume:	20 µl			
modifier volume:	5 µl			
diluent volume:	5 µl			
Signal measurement:	peak area			
number of replicates:	3 (samples and standards)			

modifier mixture: 5 ml $NH_4H_2PO_4$ (100 g/l) and 3 ml $Mg(NO_3)_2$-solution (10 g/l) are transferred to a calibrated 50 ml quartz flask and made up to volume with pure water.

Standard solutions:
lead-standard: 1000 mg/l Pb, BAKER INSTRA-ANALYZED
cadmium-standard: 1000 mg/l Cd, BAKER INSTRA-ANALYZED
The standards are accurate to within 0,2 % and are traceable to NIST.

Furnace programme:

Step	Temp [°C]	Ramp Time	Hold Time	Internal Flow	Read Step	Gas Type
1	110	1	40	250		Normal
2	130	30	30	250		Normal
3	500	20	30	250		Normal
4	1500	0	5	0	*	Normal
5	2500	1	5	250		Normal

Calibration range:

	Cd	Pb
linear range	0.1 – 2 ppb	1 – 20 ppb
Calibration curve	y = b*x + a	
slope (b)	0.0078	0.0034
intercept (a)	0.00122	0.0021

5.2 Arsenic, Nickel – GF-AAS

lamps:	As: electrodeless discharge lamp (EDL)			
	Ni: hollow cathode lamp (HKL)			
wavelength:	As:	193.7 nm	Ni	232.0 nm
current:	As	400 mA	Ni	25 mA
gas:	Argon			
background correction:	Zeeman			
sample volume:	20 µl			
modifier volume	5 µl			
diluent volume:	5 µl			
signal measurement:	peak area			
number of replicates:	3 (samples and standards)			

modifier mixture : 5 ml $Pd(NO_3)_2$ (10 g/l) and 3 ml $Mg(NO_3)_2$-solution (10 g/l) are transferred to a calibrated 50 ml quartz flask and made up to volume with pure water .

Standard solutions:
arsenic-standard: 1000 mg/l As, BAKER INSTRA-ANALYZED
nickel-standard: 1000 mg/l Ni, BAKER INSTRA-ANALYZED
The standards are accurate to within 0,2 % and are traceable to NIST.

Furnace programme:

Step	Temp [°C]	Ramp Time	Hold Time	Internal Flow	Read Step	Gas Type
1	110	1	30	250		Normal
2	130	20	30	250		Normal
3	1250	10	20	250		Normal
4	2300	0	6	0	*	Normal
5	2500	1	7	250		Normal

Calibration range:

	As	Ni

linear range	1 – 20 ppb	1 – 20 ppb
Calibration curve	y = b*x + a	
slope (b)	0.0039	0.0045
intercept (a)	-0.00015	0.0036

6 WORK PROGRAMME

The UBA lab received 40 real filters and 4 field filter blanks from the Instituto de Salud Carlos.
One digestion run included the digestion of 4 real filters, 1 reagent blank or 1 filter blank and 1 reference material (NIST 1648 or NIES No.8). Portions of 10 mg NIST 1648 and of 80 mg NIES No.8 were used for the digestion. The reference material was digested without a filter.

7 QA/QC PROCEDURE

4 QC samples (every 10^{th} sample)
recovery measurements (every 10^{th} sample)
reference material 1648 NIST (each day NIST 1648, which was digested at the beginning of the MVP is measured)

8 RESULTS

The results are in an excel file, called ANNEX_WG14_MadridFWork_lab D.xls

REPORT OF LAB D (using ICP mass)

Short Report on the

Field Test in Madrid
of the Minimum Validation Programme for a
"Reference Method for the Determination of Pb, Cd, As and Ni in Ambient Air"
(CEN / TC 264 / WG 14)

Voluntary contribution, performed by Lab. D, UBA-Germany

The samples (digested and previously analysed using AAS by Lab D, UBA-Wien) were reanalysed in our lab using ICP/MS-technique. Before analysis, the samples were diluted with $H_2O_{demin.}$ and internal standards were added. However, the blank values presented in the result sheet are recalculated to the original dilution (50 mL) and thus are directly comparable to the results of Lab D, UBA-Wien. The analytical conditions used are given below.

1 Analytical conditions :

Analysis performed : 20.08. – 28.08.01

Instrument : ICP/MS, type : Ultramass, producer : Varian

Masses monitored :

In	115	Sc	45
As	75	Ni	60
Cd	111	Pb	208

Calibration :

The same calibration was used for samples, blanks and CRM-solutions, but solutions were diluted differently before analysis :

Samples and blanks : dilution factor 2
NIST 1648 : dilution factor 20
NIES No.8 : dilution factor 10

Internal standards : In 10 µg/L (As, Cd, Pb),
Sc 10 µg/L (Ni)

External calibration standards :

-standard blank solution
-operating standard-1 solution (element conc. : 20 µg/L As, Pb, Cd, Ni)
-operating standard-2 solution (element conc. : 100 µg/L As, Pb, Cd, Ni)

2 RESULTS

The results is in an excel file, called ANNEX_WG14_Madrid FW_lab D-ICP.xls

Instituto de Salud Carlos III

Ministerio de Sanidad y Consumo
Centro Nacional de Sanidad Ambiental

Area de Contaminación Atmosférica

COMPARISON OF THE 4 (AAS) + 2 (ICP) LABORATORY RESULTS

On the following tables, the results of the 4 laboratories which used AAS and the laboratories which the ICP technique was utilised are displayed.

Comparison of the analytical results for Lead (with Lab D- ICP)

Pb ng/m3	Lab A		Lab B		Lab C		Lab D		Lab D-ICP	
Day	SP-01	SP-02	SP-08	SP-10	SP-05	SP-07	SP-03	SP-04	SP-03	SP-04
4-5-01	22,63	24,86	14,76	29,65	30,70	28,52	24,88	26,81	24,82	25,99
5-5-01	18,96	16,18	24,94	26,14	23,59	25,11	21,13	23,20	21,76	22,69
6-5-01	17,71	17,43	21,76	23,70	20,93	21,72	18,01	20,44	16,67	20,20
7-5-01	33,15	29,84	33,20	34,11	35,65	35,97	31,21	32,66	31,19	32,20
8-5-01	31,56	32,32	34,45	34,69	34,43	36,90	32,11	32,89	32,29	31,21
10-5-01	35,84	33,86	38,42	37,70	38,85	39,11	36,77	37,61	36,10	36,68
12-5-01	18,28	17,55	20,49	19,72	19,05	19,93	19,12	18,82	19,64	18,53
13-5-01	8,31	7,56	8,68	8,57	9,72	10,29	8,66	8,73	8,31	8,75
14-5-01	11,81	12,37	12,74	9,45	13,92	13,57	12,72	9,45	13,08	9,08
15-5-01	9,67	11,42	9,96	12,13	10,58	10,24	10,18	12,69	10,37	12,58
16-5-01	13,60	13,69	13,74	13,49	15,09	16,11	13,97	13,53	14,65	13,47
17-5-01	19,87	13,55	19,39	18,75	20,10	21,49	16,93	18,18	17,89	17,97
18-5-01	23,42	19,67	24,50	23,21	23,96	22,50	21,25	22,23	21,46	22,13
19-5-01	21,26	19,03	24,47	23,96	24,44	22,16	23,28	24,10	23,56	25,77
20-5-01	26,76	24,64	29,35	27,82	33,90	29,74	32,96	29,99	32,49	27,17
21-5-01	33,16	24,47	35,48	33,80	35,70	34,54	34,68	38,70	33,95	40,37
22-5-01	41,85	43,91	42,94	42,57	44,64	43,63	43,57	51,34	42,46	57,49
23-5-01	26,35	26,08	30,26	29,54	29,71	30,58	29,46	29,60	55,19	28,71
24-5-01	32,83	31,82	37,11	36,82	37,71	36,29	36,18	43,50	37,08	37,07
25-5-01	28,85	38,91	35,13	35,34	34,95	37,88	33,42	35,09	35,59	33,91

Comparison of the analytical results for Lead (with Lab B- ICP)

Pb ng/m3	Lab A		Lab B		Lab B - ICP		Lab C		Lab D	
Day	SP-01	SP-02	SP-08	SP-10	SP-08	SP-10	SP-05	SP-07	SP-03	SP-04
4-5-01	22,63	24,86	14,76	29,65	15,47	31,38	30,70	28,52	24,88	26,81
5-5-01	18,96	16,18	24,94	26,14	26,65	27,33	23,59	25,11	21,13	23,20
6-5-01	17,71	17,43	21,76	23,70	22,22	24,44	20,93	21,72	18,01	20,44
7-5-01	33,15	29,84	33,20	34,11	36,34	36,99	35,65	35,97	31,21	32,66
8-5-01	31,56	32,32	34,45	34,69	36,10	38,42	34,43	36,90	32,11	32,89
10-5-01	35,84	33,86	38,42	37,70	41,95	41,87	38,85	39,11	36,77	37,61
12-5-01	18,28	17,55	20,49	19,72	21,38	21,05	19,05	19,93	19,12	18,82
13-5-01	8,31	7,56	8,68	8,57	9,57	9,89	9,72	10,29	8,66	8,73
14-5-01	11,81	12,37	12,74	9,45	14,61	10,72	13,92	13,57	12,72	9,45
15-5-01	9,67	11,42	9,96	12,13	11,42	14,15	10,58	10,24	10,18	12,69
16-5-01	13,60	13,69	13,74	13,49	16,22	15,73	15,09	16,11	13,97	13,53
17-5-01	19,87	13,55	19,39	18,75	20,80	20,33	20,10	21,49	16,93	18,18
18-5-01	23,42	19,67	24,50	23,21	26,40	24,46	23,96	22,50	21,25	22,23
19-5-01	21,26	19,03	24,47	23,96	26,83	26,22	24,44	22,16	23,28	24,10
20-5-01	26,76	24,64	29,35	27,82	31,78	32,11	33,90	29,74	32,96	29,99
21-5-01	33,16	24,47	35,48	33,80	39,21	38,55	35,70	34,54	34,68	38,70
22-5-01	41,85	43,91	42,94	42,57	51,80	49,53	44,64	43,63	43,57	51,34
23-5-01	26,35	26,08	30,26	29,54	29,65	32,91	29,71	30,58	29,46	29,60
24-5-01	32,83	31,82	37,11	36,82	40,02	40,72	37,71	36,29	36,18	43,50
25-5-01	28,85	38,91	35,13	35,34	36,21	38,78	34,95	37,88	33,42	35,09

Blanc values for lead (ng/m^3) (with Lab D- ICP)

Pb Blank	Lab A		Lab B		Lab C		Lab D		Lab D-ICP	
	ug/l	ng/m3	ug/l	ng/m3	ug/l	ng/m3	ug/l	ng/m3	ug/l	ng/m3
Reagent B-1	0,70	0,64	1,52	1,38	***0,20***	0,18	0,31	0,28	3,28	2,98
Reagent B-2	0,30	0,27	0,34	0,31	***0,22***	0,20	0,09	0,08	0,28	0,26
Reagent B-3	0,40	0,36	0,3	0,27	***0,43***	0,39	0,78	0,71	1,05	0,95
Reagent B-4	0,20	0,18	14	12,73	***0,78***	0,71	0,32	0,29	0,51	0,46
Lab Filter B-1			0,26	0,24	***0,32***	0,29	0,70	0,63	3,20	2,91
Lab Filter B-2			0,18	0,16	***0,60***	0,55	0,80	0,73	1,23	1,12
Lab Filter B-3			0,7	0,64	***1,11***	1,01	1,03	0,94	3,16	2,87
Lab Filter B-4			0,18	0,16	***0,58***	0,53	1,12	1,02	3,58	3,25
Field Filter B-1	0,10	0,09	0,24	0,22	***0,14***	0,13	0,85	0,77	1,05	0,95
Field Filter B-2	0,20	0,18	0,14	0,13	***0,41***	0,37	0,56	0,50	2,33	2,12
Field Filter B-3	0,40	0,36	0,14	0,13	***0,27***	0,25	0,37	0,34	0,86	0,78
Field Filter B-4	0,80	0,73	0,14	0,13	***0,05***	0,05	1,24	1,13	1,53	1,39
	< detection limit									

Blanc values for lead (ng/m^3) (with Lab B- ICP)

Pb Blank	Lab A		Lab B		Lab B -ICP		Lab C		Lab D	
	ug/l	ng/m3	ug/l	ng/m3	ug/l	ng/m3	ug/l	ng/m3	ug/l	ng/m3
Reagent B-1	0,70	0,64	1,52	1,38	1,39	1,26	***0,20***	0,18	0,31	0,28
Reagent B-2	0,30	0,27	0,34	0,31	0,38	0,35	***0,22***	0,20	0,09	0,08
Reagent B-3	0,40	0,36	0,3	0,27	0,33	0,30	***0,43***	0,39	0,78	0,71
Reagent B-4	0,20	0,18	14	12,73	0,32	0,29	***0,78***	0,71	0,32	0,29
Lab Filter B-1	0,60	0,55	0,26	0,24	0,33	0,30	***0,32***	0,29	0,70	0,63
Lab Filter B-2	0,36	0,33	0,18	0,16	0,20	0,18	***0,60***	0,55	0,80	0,73
Lab Filter B-3	0,40	0,36	0,7	0,64	0,56	0,51	***1,11***	1,01	1,03	0,94
Lab Filter B-4	0,20	0,18	0,18	0,16	0,22	0,20	***0,58***	0,53	1,12	1,02
Field Filter B-1	0,10	0,09	0,24	0,22	0,28	0,26	***0,14***	0,13	0,85	0,77
Field Filter B-2	0,20	0,18	0,14	0,13	0,17	0,15	***0,41***	0,37	0,56	0,50
Field Filter B-3	0,40	0,36	0,14	0,13	0,19	0,17	***0,27***	0,25	0,37	0,34
Field Filter B-4	0,80	0,73	0,14	0,13	0,21	0,19	***0,05***	0,05	1,24	1,13
	< detection limit									

Recovery rates for lead (with Lab D- ICP)

Pb recovery	Lab A		Lab B		Lab C		Lab D		Lab D-ICP	
6550 +/- 80	mg/kg	recovery %	weigh mg/kg	recovery %	weigh mg/kg	recovery %	weigh mg/kg	recovery %	weigh mg/kg	recovery %
NIST-1	6530,0	99,7	7080,9	108,1	6272,0	95,8	6473,7	98,8	6625,5	101,2
NIST-1	6524,0	99,6	6214,4	94,9	6526,0	99,6	6182,0	94,4	5832,0	89,0
NIST-1	6189,0	94,5	6714	102,5	6506,0	99,3	6157,9	94,0	6272,1	95,8
NIST-1	6229,0	95,1	6749,8	103,1	6438,0	98,3	6281,4	95,9	6367,4	97,2
mean	6368,0	97,2	6689,8	102,1	6435,5	98,3	6273,8	95,8	6274,2	95,8
Sd	184,3	2,8	357,4	5,5	115,3	1,8	143,6	2,2	330,5	5,0
RSD (%)	2,9	2,9	5,3	5,3	1,8	1,8	2,3	2,3	5,3	5,3
219 +/- 9										
NIES-1	230	105,0	242,0	110,5	214,6	98,0	218,1	99,6	218,1	99,6
NIES-2	224	102,3	233,1	106,4	221,8	101,3	236,8	108,1	248,5	113,5
NIES-3	228	104,1	251,3	114,8	221,8	101,3	209,1	95,5	231,5	105,7
NIES-4	225	102,7	242,1	110,5	223,0	101,8	215,9	98,6	234,5	107,1
mean	226,8	103,5	242,1	110,6	220,3	100,6	220,0	100,4	233,1	106,5
Sd	2,8	1,3	7,4	3,4	3,8	1,8	11,9	5,4	12,5	5,7
RSD (%)	1,2	1,2	3,1	3,1	1,7	1,7	5,4	5,4	5,4	5,4

Recovery rates for lead (with Lab B- ICP)

Pb recovery	Lab A		Lab B		Lab B - ICP		Lab C		Lab D	
6550 +/- 80	mg/kg	recovery %	weigh mg/kg	recovery %	weigh mg/kg	recovery %	weigh mg/kg	recovery %	weigh mg/kg	recovery %
NIST-1	6530,0	99,7	7080,9	108,1	6550,9	100,0	6272,0	95,8	6473,7	98,8
NIST-1	6524,0	99,6	6214,4	94,9	5759,6	87,9	6526,0	99,6	6182,0	94,4
NIST-1	6189,0	94,5	6714	102,5	6328,0	96,6	6506,0	99,3	6157,9	94,0
NIST-1	6229,0	95,1	6749,8	103,1	6438,1	98,3	6438,0	98,3	6281,4	95,9
mean	6368,0	97,2	6689,8	102,1	6269,2	95,7	6435,5	98,3	6273,8	95,8
Sd	184,3	2,8	357,38	5,5	351,7	5,4	115,3	1,8	143,6	2,2
RSD (%)	2,9	2,9	5,3422	5,3	5,6	5,6	1,8	1,8	2,3	2,3
219 +/- 9										
NIES-1	230	105,0	242,0	110,5	219,7	100,3	214,6	98,0	218,1	99,6
NIES-2	224	102,3	233,1	106,4	216,8	99,0	221,8	101,3	236,8	108,1
NIES-3	228	104,1	251,3	114,8	234,3	107,0	221,8	101,3	209,1	95,5
NIES-4	225	102,7	242,1	110,5	230,5	105,3	223,0	101,8	215,9	98,6
mean	226,8	103,5	242,1	110,6	225,3	102,9	220,3	100,6	220,0	100,4
Sd	2,8	1,3	7,4	3,4	8,4	3,8	3,8	1,8	11,9	5,4
RSD (%)	1,2	1,2	3,1	3,1	3,7	3,7	1,7	1,7	5,4	5,4

Analytical results for Cadmium (ng/m^3) (with Lab D- ICP)

Cd ng/m3	Lab A		Lab B		Lab C		Lab D		Lab D-ICP	
Day	SP-01	SP-02	SP-08	SP-10	SP-05	SP-07	SP-03	SP-04	SP-03	SP-04
4-5-01	0,09	0,08	0,08	0,16	0,25	0,18	0,12	0,13	0,13	0,15
5-5-01	n.d.	0,01	0,15	0,10	0,09	0,10	0,05	0,06	0,07	0,08
6-5-01	0,07	0,02	0,07	0,16	0,10	0,12	0,08	0,09	0,09	0,10
7-5-01	0,23	0,15	0,22	0,28	0,26	0,27	0,21	0,29	0,25	0,31
8-5-01	0,20	0,18	0,23	0,28	0,26	0,29	0,21	0,22	0,23	0,24
10-5-01	0,19	0,16	0,30	0,87	0,28	0,28	0,22	0,22	0,21	0,28
12-5-01	0,11	0,08	0,20	0,24	0,26	0,33	0,16	0,16	0,18	0,18
13-5-01	0,05	0,03	0,12	0,13	0,15	0,14	0,09	0,11	0,09	0,13
14-5-01	0,89	0,94	0,74	0,30	1,00	0,93	0,93	0,16	0,95	0,20
15-5-01	0,12	0,11	0,22	3,86	0,21	0,20	0,18	0,93	0,22	1,00
16-5-01	0,86	0,89	0,72	0,72	0,98	1,00	0,91	0,89	0,98	0,94
17-5-01	0,74	0,71	0,67	0,69	0,85	0,84	0,80	0,88	0,89	0,93
18-5-01	0,03	0,07	0,14	0,16	0,14	0,13	0,09	0,10	0,13	0,13
19-5-01	0,05	0,06	0,12	0,15	0,13	0,11	0,08	0,08	0,10	0,11
20-5-01	0,26	0,28	0,33	0,35	0,39	0,38	0,31	0,34	0,34	0,34
21-5-01	1,00	0,87	0,84	0,81	1,15	1,15	1,12	1,18	1,19	1,25
22-5-01	0,58	0,60	0,58	0,60	0,74	0,68	0,64	0,84	0,68	1,04
23-5-01	0,17	0,17	0,39	0,26	0,24	0,27	0,22	0,21		0,25
24-5-01	0,29	0,14	0,24	0,41	0,43	0,41	0,38	0,37	0,48	0,37
25-5-01	0,24	0,10	0,33	0,24	0,27	0,29	0,21	0,21	0,30	0,22

Analytical results for Cadmium (ng/m^3) (with Lab B- ICP)

Cd ng/m3	Lab A		Lab B		Lab B - ICP		Lab C		Lab D	
Day	SP-01	SP-02	SP-08	SP-10	SP-08	SP-10	SP-05	SP-07	SP-03	SP-04
4-5-01	0,09	0,08	0,08	0,16	0,15	0,16	0,25	0,18	0,12	0,13
5-5-01	n.d.	0,01	0,15	0,10	0,16	0,07	0,09	0,10	0,05	0,06
6-5-01	0,07	0,02	0,07	0,16	0,08	0,12	0,10	0,12	0,08	0,09
7-5-01	0,23	0,15	0,22	0,28	0,23	0,26	0,26	0,27	0,21	0,29
8-5-01	0,20	0,18	0,23	0,28	0,24	0,24	0,26	0,29	0,21	0,22
10-5-01	0,19	0,16	0,30	0,87	0,32	1,19	0,28	0,28	0,22	0,22
12-5-01	0,11	0,08	0,20	0,24	0,19	0,18	0,26	0,33	0,16	0,16
13-5-01	0,05	0,03	0,12	0,13	0,10	0,10	0,15	0,14	0,09	0,11
14-5-01	0,89	0,94	0,74	0,30	0,98	0,28	1,00	0,93	0,93	0,16
15-5-01	0,12	0,11	0,22	3,86	0,22	4,91	0,21	0,20	0,18	0,93
16-5-01	0,86	0,89	0,72	0,72	0,95	0,90	0,98	1,00	0,91	0,89
17-5-01	0,74	0,71	0,67	0,69	0,87	0,83	0,85	0,84	0,80	0,88
18-5-01	0,03	0,07	0,14	0,16	0,13	0,12	0,14	0,13	0,09	0,10
19-5-01	0,05	0,06	0,12	0,15	0,11	0,11	0,13	0,11	0,08	0,08
20-5-01	0,26	0,28	0,33	0,35	0,34	0,33	0,39	0,38	0,31	0,34
21-5-01	1,00	0,87	0,84	0,81	1,18	1,07	1,15	1,15	1,12	1,18
22-5-01	0,58	0,60	0,58	0,60	0,72	0,65	0,74	0,68	0,64	0,84
23-5-01	0,17	0,17	0,39	0,26	0,33	0,23	0,24	0,27	0,22	0,21
24-5-01	0,29	0,14	0,24	0,41	0,44	0,52	0,43	0,41	0,38	0,37
25-5-01	0,24	0,10	0,33	0,24	0,37	0,20	0,27	0,29	0,21	0,21

Blanc values for Cadmium (ng/m^3) (with Lab D- ICP)

Cd Blank values	Lab A		LabB		Lab C		Lab D		Lab D-ICP	
	ug/l	ng/m3	ug/l	ng/m3	ug/l	ng/m3	ug/l	ng/m3	ug/l	ng/m3
Reagent B-1	0,04	0,04	0,10	0,09	***0,04***	0,04	-0,01	-0,01	0,11	0,10
Reagent B-2	0,04	0,04	0,10	0,09	***0,04***	0,04	-0,01	-0,01	0,01	0,01
Reagent B-3	0,06	0,05	0,06	0,05	0,06	0,05	0,01	0,01	0,04	0,04
Reagent B-4	0,01	0,01	0,04	0,03	0,06	0,05	0,00	0,00	0,03	0,03
Lab Filter B-1	-0,02	-0,02	0,05	0,05	***0,04***	0,03	-0,01	0,00	0,09	0,08
Lab Filter B-2	-0,03	-0,03	0,04	0,03	***0,04***	0,03	0,00	0,00	0,02	0,02
Lab Filter B-3	-0,03	-0,03	0,05	0,04	***0,03***	0,02	0,05	0,04	0,16	0,14
Lab Filter B-4	-0,04	-0,04	0,04	0,04	0,07	0,06	0,00	0,00	0,09	0,08
Field Filter B-1	-0,03	-0,03	0,03	0,03	***0,03***	0,03	0,00	0,00	0,02	0,02

Field Filter B-2	-0,09	-0,08	0,03	0,03	0,06	0,06	0,02	0,02	0,10	0,09
Field Filter B-3	-0,02	-0,02	0,04	0,03	***0,04***	0,03	0,00	0,00	0,01	0,01
Field Filter B-4	-0,06	-0,05	0,06	0,06	***0,04***	0,04	0,02	0,02	0,05	0,04
	< detection limit									

Blanc values for Cadmium (ng/m^3) (with Lab B- ICP)

Cd Blank values	**Lab A**		**Lab B**		**Lab B -ICP**		**Lab C**		**Lab D**	
	ug/l	**ng/m3**	**ug/l**	**ng/m3**	**ug/l**	**ng/m3**	**ug/l**	**ng/m3**	**ug/l**	**ng/m3**
Reagent B-1	0,04	0,04	0,10	0,09	0,07	0,06	***0,04***	0,04	-0,01	-0,01
Reagent B-2	0,04	0,04	0,10	0,09	0,06	0,05	***0,04***	0,04	-0,01	-0,01
Reagent B-3	0,06	0,05	0,06	0,05	0,05	0,05	0,06	0,05	0,01	0,01
Reagent B-4	0,01	0,01	0,04	0,03	0,03	0,03	0,06	0,05	0,00	0,00
Lab Filter B-1	-0,02	-0,02	0,05	0,05	0,02	0,02	***0,04***	0,03	-0,01	0,00
Lab Filter B-2	-0,03	-0,03	0,04	0,03	0,01	0,01	***0,04***	0,03	0,00	0,00
Lab Filter B-3	-0,03	-0,03	0,05	0,04	0,03	0,03	***0,03***	0,02	0,05	0,04
Lab Filter B-4	-0,04	-0,04	0,04	0,04	0,01	0,01	0,07	0,06	0,00	0,00
Field Filter B-1	-0,03	-0,03	0,03	0,03	0,01	0,01	***0,03***	0,03	0,00	0,00
Field Filter B-2	-0,09	-0,08	0,03	0,03	0,01	0,01	0,06	0,06	0,02	0,02
Field Filter B-3	-0,02	-0,02	0,04	0,03	0,01	0,01	***0,04***	0,03	0,00	0,00
Field Filter B-4	-0,06	-0,05	0,06	0,06	0,01	0,01	***0,04***	0,04	0,02	0,02
	< detection limit									

Recovery rates for Cadmium (with Lab D- ICP)

Cd recovery	**Lab A**		**Lab B**		**Lab C**		**Lab D**		**Lab D-ICP**	
75 +/- 7	**mg/kg**	**recovery %**	**mg/kg**	**recovery %**	**mg/kg**	**recovery %**	**mg/kg**	**recovery %**	**mg/kg**	**recovery %**
NIST-1	71,3	95,0	53,3	71,1	70,1	93,5	78,2	104,2	75,7	101,0
NIST-1	73,8	98,3	53,4	71,2	71,9	95,8	68,3	91,1	67,4	89,9
NIST-1	72,9	97,2	73,7	98,3	69,9	93,1	68,4	91,3	69,9	93,2
NIST-1	70,8	94,4	76,0	101,3	69,2	92,2	69,7	92,9	73,3	97,8
mean	72,2	96,3	64,1	85,5	70,2	93,7	71,2	94,9	71,6	95,5
Sd	1,4	1,8	12,4	16,6	1,1	1,5	4,7	6,3	3,7	4,9
RSD (%)	1,9	1,9	19,4	19,4	1,6	1,6	6,6	6,6	5,1	5,1
1.1 +/- 0,1										
NIES-1	1,06	96,4	0,9	79,4	1,1	100,9	1,0	91,4	1,1	97,7
NIES-2	1,04	94,5	0,9	78,9	1,2	110,9	1,2	108,8	1,4	127,8
NIES-3	1,02	92,7	0,9	83,3	1,0	91,8	1,0	89,5	1,2	108,9
NIES-4	1,20	109,1	1,0	87,4	1,0	92,7	1,0	87,6	1,2	111,5
mean	1,1	98,2	0,9	82,2	1,1	99,1	1,0	94,3	1,2	111,5

Sd	0,1	7,4	0,0	4,0	0,1	8,9	0,1	9,8	0,1	12,4
RSD (%)	7,6	7,6	4,8	4,8	9,0	9,0	10,4	10,4	11,2	11,2

Recovery rates for Cadmium (with Lab B- ICP)

Cd recovery	Lab A		Lab B		Lab B - ICP		Lab C		Lab D	
75 +/- 7	mg/kg	recovery %	mg/kg	recovery %	mg/kg	recovery %	mg/kg	recovery %	mg/kg	recovery %
NIST-1	71,3	95,0	53,3	71,1	85,6	114,2	70,1	93,5	78,2	104,2
NIST-1	73,8	98,3	53,4	71,2	68,6	91,5	71,9	95,8	68,3	91,1
NIST-1	72,9	97,2	73,7	98,3	75,0	100,0	69,9	93,1	68,4	91,3
NIST-1	70,8	94,4	76,0	101,3	76,4	101,9	69,2	92,2	69,7	92,9
mean	72,2	96,3	64,1	85,5	76,4	101,9	70,2	93,7	71,2	94,9
Sd	1,4	1,8	12,4	16,6	7,0	9,4	1,1	1,5	4,7	6,3
RSD (%)	1,9	1,9	19,4	19,4	9,2	9,2	1,6	1,6	6,6	6,6
1.1 +/- 0,1										
NIES-1	1,1	96,4	0,9	79,4	1,0	95,0	1,1	100,9	1,0	91,4
NIES-2	1,0	94,5	0,9	78,9	1,1	100,2	1,2	110,9	1,2	108,8
NIES-3	1,0	92,7	0,9	83,3	1,2	108,6	1,0	91,8	1,0	89,5
NIES-4	1,2	109,1	1,0	87,4	1,2	104,9	1,0	92,7	1,0	87,6
mean	1,1	98,2	0,9	82,2	1,1	102,2	1,1	99,1	1,0	94,3
Sd	0,1	7,4	0,0	4,0	0,1	5,9	0,1	8,9	0,1	9,8
RSD (%)	7,6	7,6	4,8	4,8	5,8	5,8	9,0	9,0	10,4	10,4

Recovery rates for Cadmium (with Lab B- ICP)

Cd recovery	Lab A		Lab B		Lab B - ICP		Lab C		Lab D	
75 +/- 7	mg/kg	recovery %	mg/kg	recovery %	mg/kg	recovery %	mg/kg	recovery %	mg/kg	recovery %
NIST-1	71,3	95,0	53,3	71,1	85,6	114,2	70,1	93,5	78,2	104,2
NIST-1	73,8	98,3	53,4	71,2	68,6	91,5	71,9	95,8	68,3	91,1
NIST-1	72,9	97,2	73,7	98,3	75,0	100,0	69,9	93,1	68,4	91,3
NIST-1	70,8	94,4	76,0	101,3	76,4	101,9	69,2	92,2	69,7	92,9
mean	72,2	96,3	64,1	85,5	76,4	101,9	70,2	93,7	71,2	94,9
Sd	1,4	1,8	12,4	16,6	7,0	9,4	1,1	1,5	4,7	6,3
RSD (%)	1,9	1,9	19,4	19,4	9,2	9,2	1,6	1,6	6,6	6,6
1.1 +/- 0,1										
NIES-1	1,1	96,4	0,9	79,4	1,0	95,0	1,1	100,9	1,0	91,4
NIES-2	1,0	94,5	0,9	78,9	1,1	100,2	1,2	110,9	1,2	108,8
NIES-3	1,0	92,7	0,9	83,3	1,2	108,6	1,0	91,8	1,0	89,5
NIES-4	1,2	109,1	1,0	87,4	1,2	104,9	1,0	92,7	1,0	87,6
mean	1,1	98,2	0,9	82,2	1,1	102,2	1,1	99,1	1,0	94,3
Sd	0,1	7,4	0,0	4,0	0,1	5,9	0,1	8,9	0,1	9,8

RSD (%)	7,6	7,6	4,8	4,8	5,8	5,8	9,0	9,0	10,4	10,4

Analytical results for Arsenic (ng/m^3) (with Labs B- ICP and D-ICP)

As ng/m3	Lab A		Lab B-ICP		Lab C		Lab D		Lab D-ICP	
Day	SP-01	SP-02	SP-08	SP-10	SP-05	SP-07	SP-03	SP-04	SP-03	SP-04
4-5-01	0,41	0,42	0,46	0,61	0,64	0,60	0,33	0,43	0,57	1,01
5-5-01	0,33	0,22	0,66	0,64	0,59	0,57	0,49	0,66	0,65	1,56
6-5-01	0,07	0,05	0,46	0,41	0,34	0,34	0,22	0,26	0,31	0,39
7-5-01	0,56	0,75	0,89	0,89	0,91	0,86	0,75	0,80	0,85	0,56
8-5-01	0,54	0,83	0,82	0,83	0,79	0,83	0,67	0,67	0,83	0,72
10-5-01	0,49	0,66	0,94	0,87	0,86	0,99	0,73	0,77	0,80	0,90
12-5-01	0,37	0,30	0,65	0,67	0,54	0,58	0,46	0,55	0,56	0,64
13-5-01	0,13	0,33	0,31	0,33	0,25	0,20	0,18	0,21	0,10	0,37
14-5-01	0,36	0,11	0,49	0,37	0,37	0,41	0,20	0,21	0,60	0,20
15-5-01	0,20	0,24	0,41	0,43	0,34	0,38	0,21	0,27	0,38	0,33
16-5-01	0,26	0,27	0,44	0,43	0,37	0,71	0,38	0,50	0,55	0,29
17-5-01	0,70	0,46	0,84	0,79	1,47	1,76	0,89	0,89	0,84	0,69
18-5-01	0,79	0,68	0,71	0,62	1,26	1,27	0,79	0,84	0,68	0,69
19-5-01	0,35	0,20	0,53	0,55	0,64	0,42	0,48	0,35	0,35	0,44
20-5-01	0,27	0,36	0,58	0,57	0,58	0,53	0,41	0,24	0,46	0,40
21-5-01	0,26	0,24	0,71	0,69	0,78	0,91	0,68	0,54	0,63	0,58
22-5-01	0,33	0,33	0,78	0,70	1,07	1,04	0,66	0,69	0,66	0,58
23-5-01	0,52	0,43	1,01	0,85	1,58	1,64	1,03	1,04	0,90	0,91
24-5-01	1,13	0,64	1,12	1,02	2,11	2,10	1,62	1,36	1,29	0,95
25-5-01	1,29	0,90	1,02	0,95	1,46	1,34	1,06	1,09	1,14	1,05

Note: There is not AAS analysis for As by Lab B.

Blanc values for Arsenic (ng/m^3) (with Labs B- ICP and D-ICP)

As Blank values	Lab A		Lab B-ICP		Lab C		Lab D		Lab D-ICP	
	ug/l	ng/m3	ug/l	ng/m3	ug/l	ng/3	ug/l	ng/m3	ug/l	ng/m3
Reagent B-1	-0,16	-0,15	0,09	0,08	***-0,11***	-0,10	-0,14	-0,13	-0,02	-0,02

Reagent B-2	-0,2	-0,18	0,06	0,05	***-0,13***	-0,12	-0,16	-0,15	-0,01	-0,01
Reagent B-3	0,05	0,05	0,09	0,08	***-0,21***	-0,19	-0,10	-0,09	0,22	0,20
Reagent B-4	-0,34	-0,31	0,08	0,07	***-0,31***	-0,29	-0,03	-0,02	-0,11	-0,10
Lab Filter B-1	0,10	0,10	0,17	0,15	***0,09***	0,08	-0,17	-0,15	0,13	0,11
Lab Filter B-2	0,43	0,39	0,26	0,24	***0,03***	0,03	-0,17	-0,16	0,16	0,14
Lab Filter B-3	-0,54	- 0,49	0,26	0,24	***0,09***	0,08	-0,02	-0,01	0,26	0,23
Lab Filter B-4	-0,17	-0,15	0,18	0,16	***0,06***	0,05	-0,28	-0,25	0,05	0,05
Field Filter B-1	0,19	0,17	0,33	0,30	***0,04***	0,04	-0,02	-0,01	0,23	0,21
Field Filter B-2	-0,28	-0,25	0,22	0,20	***0,03***	0,03	-0,14	-0,13	-0,05	-0,05
Field Filter B-3	0,01	0,01	0,21	0,19	***-0,05***	-0,05	-0,12	-0,11	-0,09	-0,08
Field Filter B-4	-0,03	-0,03	0,25	0,22	***-0,04***	-0,03	0,03	0,03	0,04	0,04
	< detection limit									

Recovery rates for Arsenic (with Labs B- ICP and D-ICP)

As recovery	**Lab A**		**Lab B-ICP**		**Lab C**		**Lab D**		**Lab D-ICP**	
115 +/- 10	**mg/kg**	**recovery %**	**mg/kg**	**recovery %**	**mg/kg**	**recovery %**	**mg/kg**	**recovery %**	**mg/kg**	**recovery %**
NIST-1	115,0	100,0	128,2	111,5	106,6	92,7	128,0	111,3	132,2	114,9
NIST-1	117,0	101,7	111,8	97,3	124,2	108,0	123,5	107,4	113,5	98,7
NIST-1	120,0	104,3	116,7	101,5	121,3	105,5	125,1	108,8	120,8	105,0
NIST-1	128,4	111,7	119,7	104,1	117,8	102,4	127,2	110,6	118,5	103,0
mean	120,1	104,4	119,1	103,6	117,5	102,2	125,9	109,5	121,2	105,4
Sd	5,9	5,1	6,9	6,0	7,7	6,7	2,0	1,8	7,9	6,9
RSD (%)	4,9	4,9	5,8	5,8	6,6	6,6	1,6	1,6	6,5	6,5
2.6 +/- 0.2										
NIES-1	3,0	115	2,9	111,4	3,0	114,6	3,2	123,8	3,0	117,0
NIES-2	2,8	108	2,7	103,3	2,8	108,1	3,4	130,7	4,1	156,6
NIES-3	3,1	119	3,3	126,1	2,8	107,3	3,4	131,3	3,6	138,2
NIES-4	2,7	104	2,9	112,9	3,1	117,3	3,4	130,4	3,2	124,4
mean	2,9	111,5	2,9	113,4	2,9	111,8	3,4	129,0	3,5	134,0
Sd	0,2	7,0	0,2	9,4	0,1	4,9	0,1	3,5	0,5	17,4
RSD (%)	6,3	6,3	8,3	8,3	4,4	4,4	2,7	2,7	13,0	13,0

Analytical results for Nickel (ng/m^3) (with Lab D-ICP)

Ni ng/m3	**Lab A**		**Lab B**		**Lab C**		**Lab D**		**Lab D-ICP**	
Day	**SP-01**	**SP-02**	**SP-08**	**SP-10**	**SP-05**	**SP-07**	**SP-03**	**SP-04**	**SP-03**	**SP-04**
4-5-01	1,47	0,99	2,31	1,07	9,96	3,27	2,18	2,28	2,20	2,15
5-5-01	0,95	0,92	1,30	4,83	3,38	1,67	1,77	3,30	1,90	2,92
6-5-01	2,97	2,92	1,31	6,20	2,81	1,83	2,17	2,05	2,12	1,85
7-5-01	3,13	2,49	1,77	1,94	4,93	2,29	2,27	2,88	2,59	2,51
8-5-01	3,11	6,35	2,46	1,98	2,75	3,03	3,04	2,85	2,78	2,60

10-5-01	3,56	10,10	5,24	1,57	3,63	3,57	2,40	5,23	2,41	3,46
12-5-01	3,64	10,37	1,92	1,54	1,93	1,91	1,96	3,05	2,07	2,73
13-5-01	2,81	8,75	0,58	0,56	1,92	1,06	1,49	3,93	1,49	2,98
14-5-01	3,11	7,03	1,47	0,91	3,46	6,10	1,99	2,97	2,06	2,47
15-5-01	3,64	7,08	0,74	0,71	6,37	1,13	1,77	2,07	1,65	2,12
16-5-01	5,29	5,97	1,28	1,78	8,84	1,97	2,42	2,22	2,33	2,43
17-5-01	2,88	5,15	1,54	2,06	5,41	2,27	2,14	3,92	2,16	3,84
18-5-01	4,01	3,40	2,05	1,62	8,62	4,00	2,24	3,21	2,24	3,49
19-5-01	2,48	3,14	1,41	1,74	7,24	1,91	1,83	3,23	1,94	2,24
20-5-01	3,65	1,50	0,92	0,92	2,75	5,31	1,41	2,47	1,61	2,00
21-5-01	4,80	1,39	1,35	1,67	3,21	3,02	3,28	6,91	2,83	7,06
22-5-01	3,53	2,24	1,78	1,57	2,66	3,44	2,47	2,75	2,51	3,03
23-5-01	2,38	2,36	6,56	2,13	3,13	2,52	2,50	3,01	3,15	2,77
24-5-01	2,89	3,54	2,89	2,56	5,67	3,27	3,42	3,33	4,65	3,34
25-5-01	2,68	6,94	3,08	2,54	2,90	4,38	3,30		3,71	3,25

Analytical results for Nickel (ng/m^3) (with Lab B-ICP)

Ni ng/m3	**Lab A**		**Lab B**		**Lab B - ICP**		**Lab C**		**Lab D**	
Day	**SP-01**	**SP-02**	**SP-08**	**SP-10**	**SP-08**	**SP-10**	**SP-05**	**SP-07**	**SP-03**	**SP-04**
4-5-01	1,47	0,99	2,31	1,07	2,09	1,49	9,96	3,27	2,18	2,28
5-5-01	0,95	0,92	1,30	4,83	0,94	5,55	3,38	1,67	1,77	3,30
6-5-01	2,97	2,92	1,31	6,20	1,08	7,66	2,81	1,83	2,17	2,05
7-5-01	3,13	2,49	1,77	1,94	1,77	2,29	4,93	2,29	2,27	2,88
8-5-01	3,11	6,35	2,46	1,98	2,26	2,51	2,75	3,03	3,04	2,85
10-5-01	3,56	10,10	5,24	1,57	5,61	1,89	3,63	3,57	2,40	5,23
12-5-01	3,64	10,37	1,92	1,54	1,90	1,87	1,93	1,91	1,96	3,05
13-5-01	2,81	8,75	0,58	0,56	0,57	0,85	1,92	1,06	1,49	3,93
14-5-01	3,11	7,03	1,47	0,91	1,51	1,17	3,46	6,10	1,99	2,97
15-5-01	3,64	7,08	0,74	0,71	0,74	0,95	6,37	1,13	1,77	2,07
16-5-01	5,29	5,97	1,28	1,78	1,37	1,46	8,84	1,97	2,42	2,22
17-5-01	2,88	5,15	1,54	2,06	1,91	2,03	5,41	2,27	2,14	3,92
18-5-01	4,01	3,40	2,05	1,62	2,46	1,76	8,62	4,00	2,24	3,21
19-5-01	2,48	3,14	1,41	1,74	1,40	1,47	7,24	1,91	1,83	3,23
20-5-01	3,65	1,50	0,92	0,92	1,18	1,13	2,75	5,31	1,41	2,47
21-5-01	4,80	1,39	1,35	1,67	1,59	1,60	3,21	3,02	3,28	6,91
22-5-01	3,53	2,24	1,78	1,57	2,13	1,59	2,66	3,44	2,47	2,75
23-5-01	2,38	2,36	6,56	2,13	6,75	1,81	3,13	2,52	2,50	3,01
24-5-01	2,89	3,54	2,89	2,56	3,11	2,42	5,67	3,27	3,42	3,33
25-5-01	2,68	6,94	3,08	2,54	3,23	2,31	2,90	4,38	3,30	3,48

Blanc values for Nickel (ng/m^3) (with Lab D-ICP)

Ni Blank values	Lab A		Lab B		Lab C		Lab D		Lab D-ICP	
	ug/l	ng/m3	ug/l	ng/m3	ug/l	ng/m3	ug/l	ng/m3	ug/l	ng/m3
Reagent B-1	0,68	0,62	4,02	3,65	***0,35***	0,32	0,14	0,13	0,33	0,30
Reagent B-2	0,35	0,32	1,22	1,11	***0,35***	0,32	0,17	0,16	0,47	0,43
Reagent B-3	0,51	0,46	0,46	0,42	***0,44***	0,40	0,40	0,36	0,65	0,59
Reagent B-4	0,34	0,31	0,26	0,24	***0,67***	0,61	0,88	0,80	1,40	1,27
Lab Filter B-1	1,66	1,50	1,14	1,04	***1,22***	1,11	1,29	1,17	1,48	1,35
Lab Filter B-2	1,40	1,27	1,14	1,04	***1,40***	1,27	1,92	1,75	1,70	1,54
Lab Filter B-3	1,20	1,09	2,66	2,42	***1,70***	1,54	1,90	1,73	2,50	2,28
Lab Filter B-4	1,65	1,50	1,08	0,98	***0,18***	0,16	1,99	1,81	2,02	1,84
Field Filter B-1	1,83	1,66	0,66	0,60	***0,29***	0,26	1,90	1,73	1,56	1,42
Field Filter B-2	1,54	1,40	0,64	0,58	***0,85***	0,77	0,99	0,90	1,04	0,94
Field Filter B-3	1,32	1,20	0,88	0,80	***0,16***	0,14	1,22	1,11	0,99	0,90
Field Filter B-4	1,82	1,65	0,76	0,69	***0,34***	0,31	3,29	2,99	3,16	2,87
	< detection limit									

Blanc values for Nickel (ng/m^3) (with Lab B-ICP)

Ni Blank values	Lab A		Lab B		Lab B -ICP		Lab C		Lab D	
	ug/l	ng/m3	ug/l	ng/m3	ug/l	ng/m3	ug/l	ng/m3	ug/l	ng/m3
Reagent B-1	0,68	0,62	4,02	3,65	3,10	2,80	***0,35***	0,32	0,14	0,13
Reagent B-2	0,35	0,32	1,22	1,11	0,65	0,59	***0,35***	0,32	0,17	0,16
Reagent B-3	0,51	0,46	0,46	0,42	0,41	0,37	***0,44***	0,40	0,40	0,36
Reagent B-4	0,34	0,31	0,26	0,24	0,45	0,41	***0,67***	0,61	0,88	0,80
Lab Filter B-1	1,66	1,50	1,14	1,04	0,58	0,53	***1,22***	1,11	1,29	1,17
Lab Filter B-2	1,40	1,27	1,14	1,04	0,54	0,49	***1,40***	1,27	1,92	1,75

Lab Filter B-3	1,20	1,09	2,66	2,42	1,70	1,55	***1,70***	1,54	1,90	1,73
Lab Filter B-4	1,65	1,50	1,08	0,98	0,79	0,72	***0,18***	0,16	1,99	1,81
Field Filter B-1	1,83	1,66	0,66	0,60	0,73	0,67	***0,29***	0,26	1,90	1,73
Field Filter B-2	1,54	1,399	0,64	0,58	0,78	0,71	***0,85***	0,77	0,99	0,90
Field Filter B-3	1,32	1,199	0,88	0,80	1,97	1,79	***0,16***	0,14	1,22	1,11
Field Filter B-4	1,82	1,654	0,76	0,69	1,60	1,45	***0,34***	0,31	3,29	2,99
							< detection limit			

Recovery rates for Nickel (ng/m^3) (with Lab D-ICP)

Ni recovery	**Lab A**		**Lab B**		**Lab C**		**Lab D**		**Lab D-ICP**	
82 +/- 3	**mg/kg**	**recovery %**	**mg/kg**	**recovery %**	**mg/kg**	**recovery %**	**mg/kg**	**recovery %**	**mg/kg**	**recovery %**
NIST-1	72,7	88,7	77,2	94,2	76,4	93,1	76,9	93,8	76,1	92,8
NIST-1	77,2	94,1	74,6	91,0	73,1	89,2	87,7	107,0	70,0	85,3
NIST-1	74,7	91,1	76,6	93,4	74,8	91,2	82,3	100,3	80,3	97,9
NIST-1	75,6	92,2	75,2	91,7	76,0	92,6	79,0	96,3	77,9	95,0
mean	75,1	91,5	75,9	92,6	75,1	91,5	81,5	99,4	76,1	92,8
Sd	1,9	2,3	1,2	1,5	1,4	1,8	4,7	5,8	4,4	5,4
RSD (%)	2,5	2,5	1,6	1,6	1,9	1,9	5,8	5,8	5,8	5,8
18.5 +/- 1.5										
NIES-1	17,5	94,6	17,1	92,4	17,4	93,9	19,0	102,7	18,6	100,6
NIES-2	16,8	90,8	19,2	103,6	20,5	110,9	18,9	102,3	17,9	97,0
NIES-3	16,6	89,7	18,1	97,6	18,7	101,1	18,7	101,1	19,0	102,7
NIES-4	17,4	94,1	18,4	99,7	17,9	96,6	17,2	93,2	18,6	100,4
mean	17,1	92,3	18,2	98,3	18,6	100,6	18,5	99,8	18,5	100,2
Sd	0,4	2,4	0,9	4,7	1,4	7,4	0,8	4,4	0,4	2,4
RSD (%)	2,6	2,6	4,8	4,8	7,4	7,4	4,4	4,4	2,4	2,4

Recovery rates for Nickel (ng/m^3) (with Lab B-ICP)

Ni recovery	**Lab A**		**Lab B**		**Lab B - ICP**		**Lab C**		**Lab D**	
82 +/- 3	**mg/kg**	**recovery %**	**mg/kg**	**recovery %**	**mg/kg**	**recovery %**	**mg/kg**	**recovery %**	**mg/kg**	**recovery %**
NIST-1	72,7	88,7	77,25	94,2	85,3	104,0	76,4	93,1	76,9	93,8
NIST-1	77,2	94,1	74,65	91,0	85,4	104,1	73,1	89,2	87,7	107,0
NIST-1	74,7	91,1	76,60	93,4	86,3	105,2	74,8	91,2	82,3	100,3
NIST-1	75,6	92,2	75,15	91,7	86,7	105,7	76,0	92,6	79,0	96,3
mean	75,05	91,5	75,91	92,6	85,9	104,8	75,1	91,5	81,5	99,4
Sd	1,88	2,3	1,21	1,5	0,7	0,9	1,4	1,8	4,7	5,8

RSD (%)	2,50	2,5	1,60	1,6	0,8	0,8	1,9	1,9	5,8	5,8
18.5 +/- 1.5										
NIES-1	17,5	94,6	17,1	92,4	17,3	93,7	17,4	93,9	19,0	102,7
NIES-2	16,8	90,8	19,2	103,6	17,2	93,0	20,5	110,9	18,9	102,3
NIES-3	16,6	89,7	18,1	97,6	18,4	99,5	18,7	101,1	18,7	101,1
NIES-4	17,4	94,1	18,4	99,7	19,2	103,8	17,9	96,6	17,2	93,2
mean	17,1	92,3	18,2	98,3	18,0	97,5	18,6	100,6	18,5	99,8
Sd	0,4	2,4	0,9	4,7	0,9	5,1	1,4	7,4	0,8	4,4
RSD (%)	2,6	2,6	4,8	4,8	5,3	5,3	7,4	7,4	4,4	4,4

FINAL REMARKS BY LAB A

- Low concentrations below the preliminary field tests, were obtained during the Madrid field work.
- Some days, from sampling day 5th to sampling day 10th, the Nickel concentrations did not match well between sampler No 1 and sampler No 2. The same situation happened on labs C and D results.
- Both the atomisation and mineralisation temperatures for lead were different from CEN/TC 264/WG14 Document N 245 of 01-07-09. Lab C changed the mineralisation and lab D changed both temperatures. Notice, the temperature changes are on the path made by the Lab A for Cadmium where a change of the aforementioned temperatures produce an improvement of equipment sensibility. So, better results were obtained.