NPL Report COAM 20

Inter-laboratory Study of the Measurement of the Ni, As, Cd and Pb Contents of Ambient Air

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Approved on behalf of Managing Director, NPL
By D H Nettleton, Head of the Centre for Optical and Analytical Measurement

Executive summary

This report details the results of an international comparison of the measurement of the Ni, As, Cd and Pb contents on air-sampled filters and in solutions containing NIST Standard Reference Material (SRM) 1648, using either Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) or Graphite Furnace-Atomic Absorption Spectroscopy (GF-AAS) for analysis. NPL acted as the pilot laboratory for the comparison.

NPL's results showed excellent comparability with those of the other two laboratories both for analysis of a NIST SRM 1648 solution and for analysis of filter cuts from a large air-sampled filter.

This project was funded by the COAM Science Strategy Budget with the aim of benchmarking NPL's performance in a newly developed measurement capability by demonstrating comparability with established laboratories in Europe performing heavy metals analysis in ambient air.

Contents

Inter-laboratory Study of the Measurement of the Ni, As, Cd and Pb Contents of Ambient Air

Introduction

NPL invited two internationally leading analytical laboratories to participate in this comparison of the measurement of Nickel (Ni), Arsenic (As), Cadmium (Cd) and Lead (Pb) content on air-sampled filters and in solutions containing NIST SRM 1648 (Urban Particulate Matter), using either ICP-MS or GF-AAS for analysis.

The aim of this comparison was to enable NPL to assess the comparability of its relatively newly developed method, against the methods of internationally recognised ambient metals measurement laboratories and to allow the established laboratories to reaffirm their continued measurement capabilities.

The comparison was undertaken according to a mutually agreed protocol (see Appendix 1).

A set of comparison samples (see Appendix 2) was dispatched to each of the participating laboratories on 7th August 2003.

The content of the samples was unknown to the NPL analyst.

The results of analysis were received at NPL by 26th September 2003. The analysis sheets are reproduced in Appendix 3.

NPL conducted additional analyses of quality control transport standards for both the filter cuts and the NIST solution. These quality control standards had been sent to the participating laboratories along with the other samples but were returned to NPL without analysis in order to gauge whether transportation compromised the integrity of the comparison samples.

All quality control transport standards were received at NPL by 29th September 2003. The contents of these samples were not found to differ significantly from the quality control transport standards that had remained at NPL and thus it was concluded that transportation had had no significant effect on the results of the comparison.

Results and Discussion

The results are presented and discussed anonymously, as agreed with the participants. The two internationally leading analytical laboratories are referred to as Lab 2 and Lab 3. Lab 1 is NPL.

The reported mass fraction values, with measurement uncertainties at the 95% confidence level, for the four elemental analytes in the digested NIST SRM 1648 solution are shown below in Figures 1 to 4. These values have all been blank corrected, and the uncertainty in the measurement of the blank included in the final uncertainty value.

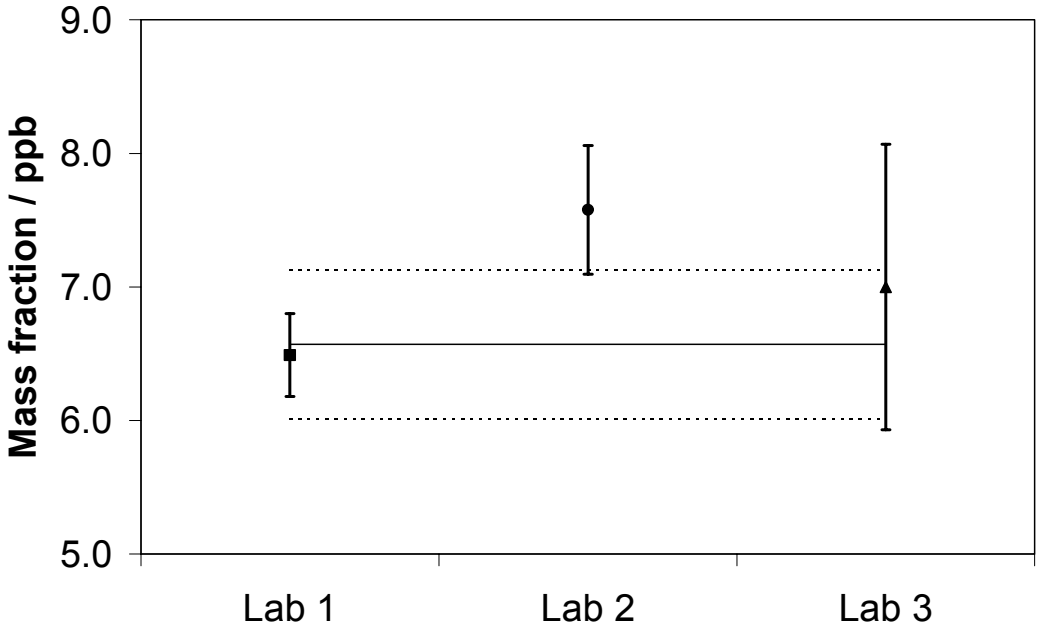


Figure 1. Nickel mass fraction measured by the three participating laboratories in the NIST SRM 1648 extract.

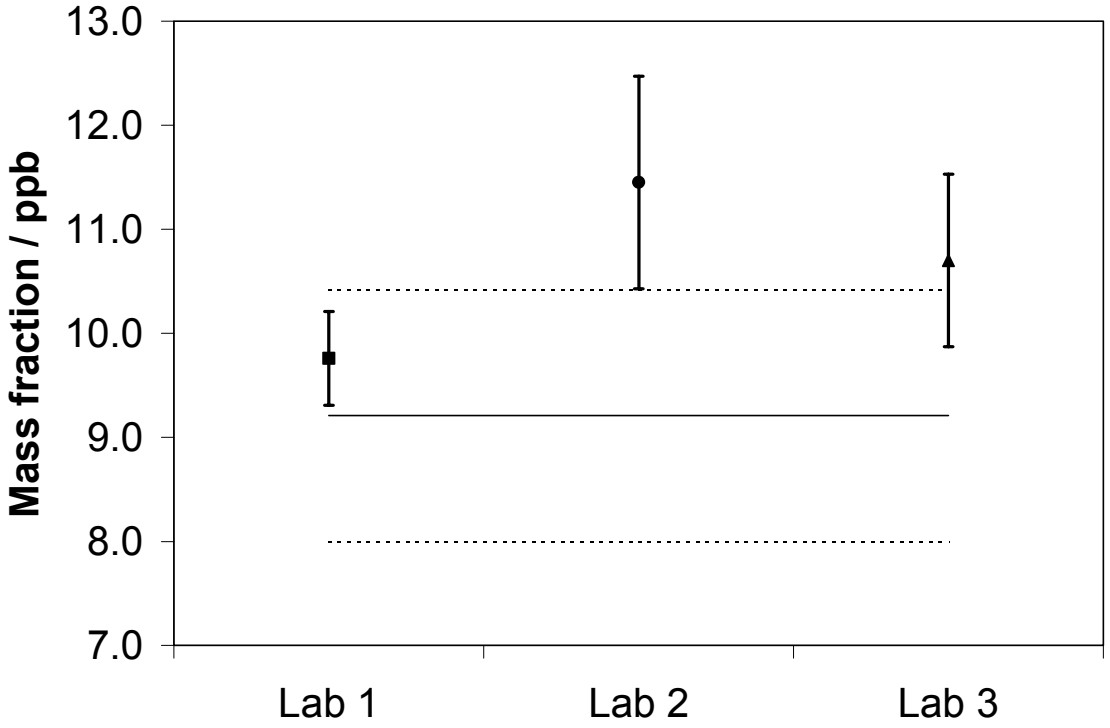


Figure 2. Arsenic mass fraction measured by the three participating laboratories in the NIST SRM 1648 extract.

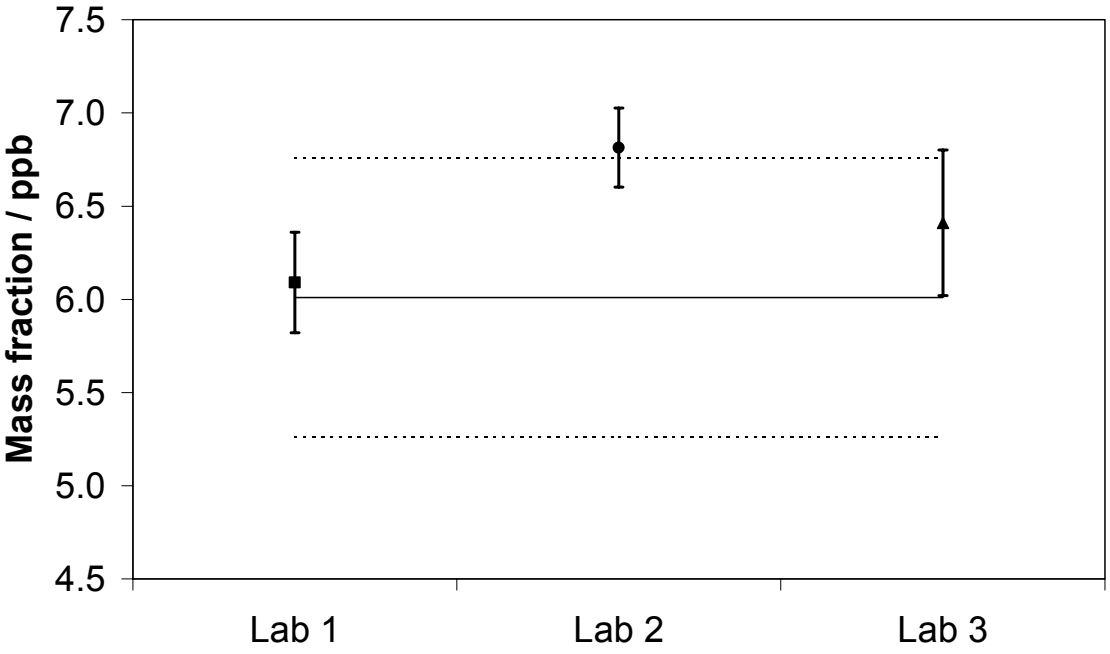


Figure 3. Cadmium mass fraction measured by the three participating laboratories in the NIST SRM 1648 extract.

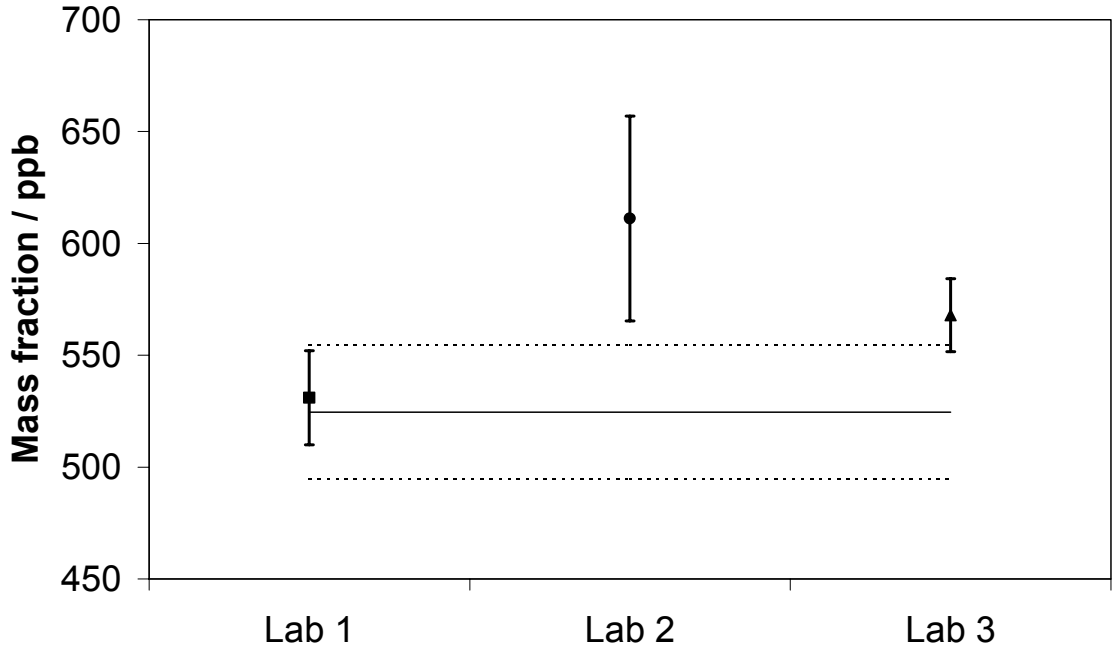


Figure 4. Lead mass fraction measured by the three participating laboratories in the NIST SRM 1648 extract.

The solid lines on each plot represent the calculated gravimetric value for the mass fraction of the NIST SRM 1648 solution, uncorrected for extraction efficiency. The dotted lines represent the uncertainty in this gravimetric value at the 95% confidence limit, including contributions from the uncertainties in the certification of the NIST material, the gravimetry of solution preparation and the variability in extraction efficiency.

In every case, except for one determination of lead content in Figure 4, the reported results are comparable with the gravimetric values as all measurement uncertainties overlap with the possible range of gravimetric values. It is interesting to note that the reported results for each analyte always show the same inter-laboratory order of numerical values, suggesting that an inter-laboratory systematic bias is present.

The reported mass values for each analyte on each individual filter cut (with measurement uncertainties at the 95% confidence level) are shown below in Figures 5 to 8.

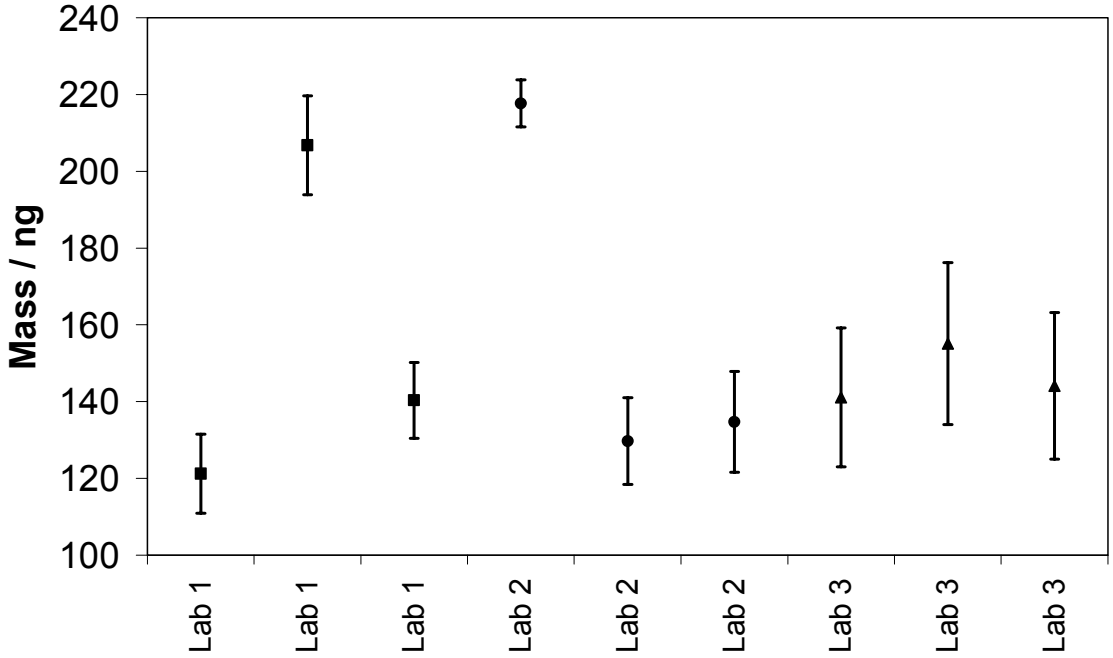
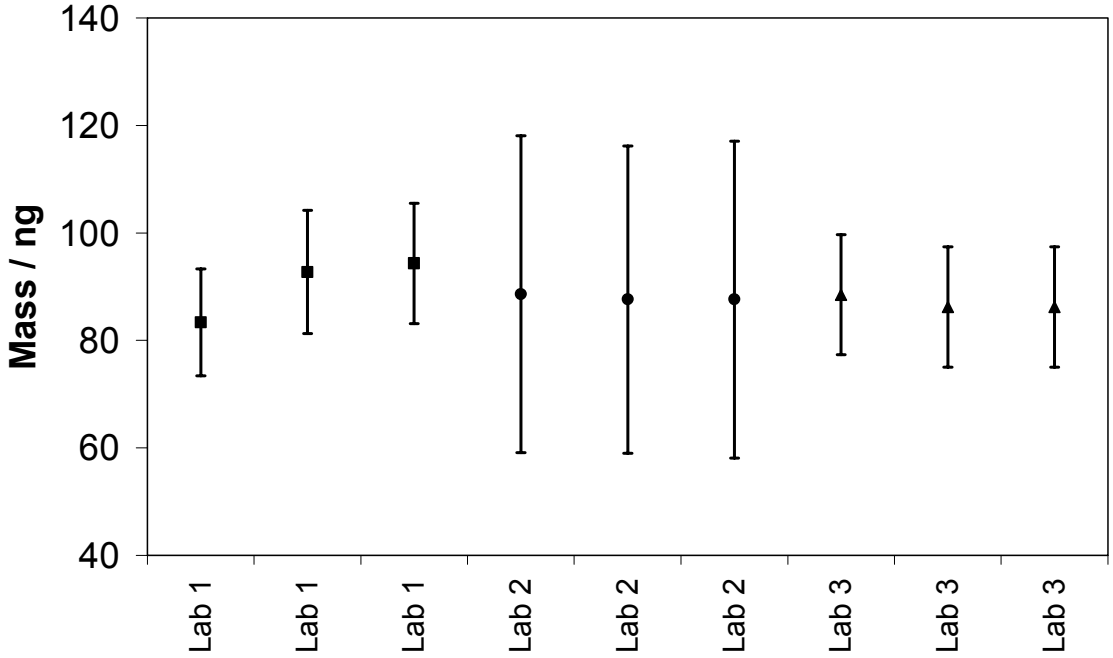


Figure 5. Mass of nickel measured on individual filter cuts by the three participating laboratories.



F**igure 6.** Mass of arsenic measured on individual filter cuts by the three participating laboratories.

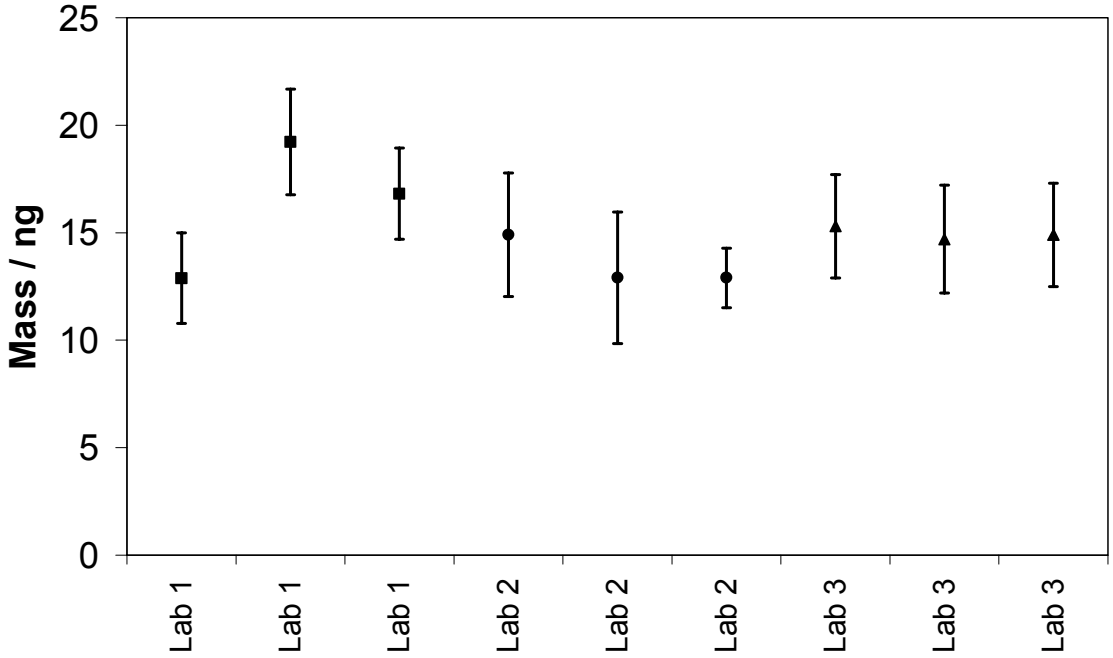


Figure 7. Mass of cadmium measured on individual filter cuts by the three participating laboratories.

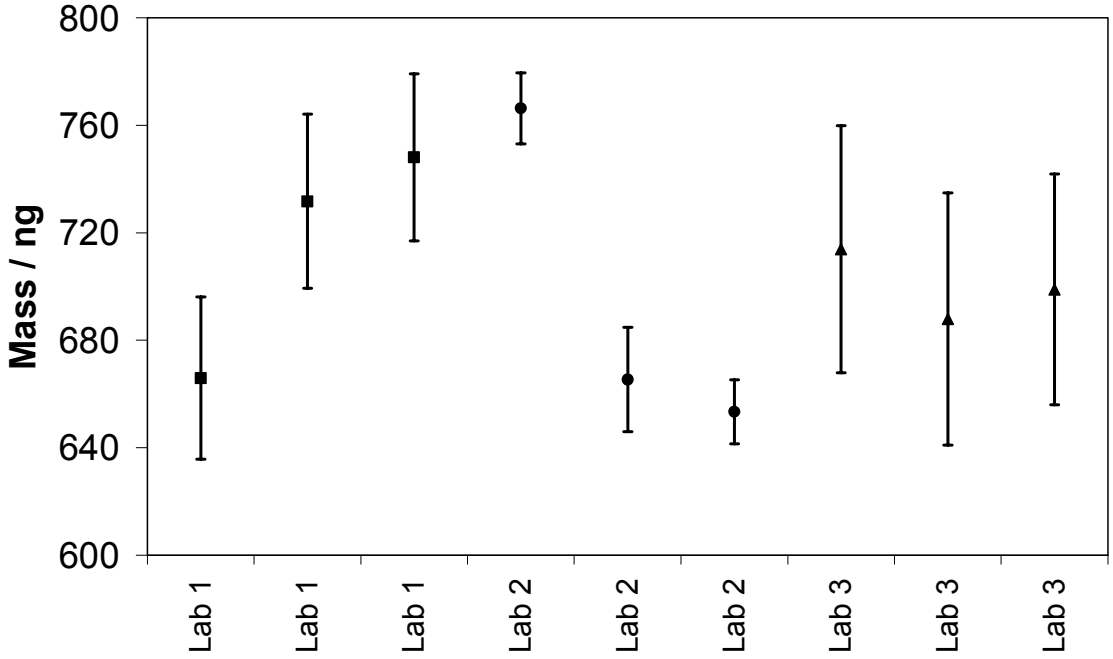


Figure 8. Mass of lead measured on individual filter cuts by the three participating laboratories.

The reported values have all been blank corrected, and the uncertainty in the measurement of the blank included in the final uncertainty value. For the purposes of the comparison it has been assumed that the inhomogeneity of the distribution of

analyte material on the sample filter is insignificant compared to the uncertainty of the analytical procedure.

No correction has been made for recovery of the analytes from the filter cuts since the average recoveries reported by each laboratory (as displayed in Appendix 4) were shown not to be significantly different from each other. In addition, the exercise was aimed at comparing results from different laboratories and not producing absolute ambient air concentration values.

The arsenic, cadmium (with one or two exceptions) and nickel (with two notable exceptions) results in Figures 5,6 and 7 show excellent comparability within the quoted measurement uncertainty both between, and within, laboratories. The inter-laboratory comparability and, with the exception of Lab 3, the intra-laboratory comparability of the lead results in Figure 8 does not appear to be as good. It is unlikely that the two outliers in the nickel determinations for Lab 1 and Lab 2 can be adequately explained by an unusually high local nickel concentration on the filter cut since the mass of the other analytes are not also anomalously high.

These reported filter cut values may be presented as an average for each laboratory, the uncertainty being reduced accordingly, and the comparability reassessed. These plots are shown below in Figures 9 to 12. The lab averages for nickel excluding the Lab 1 and Lab 2 outliers are also shown as an inset in Figure 9.

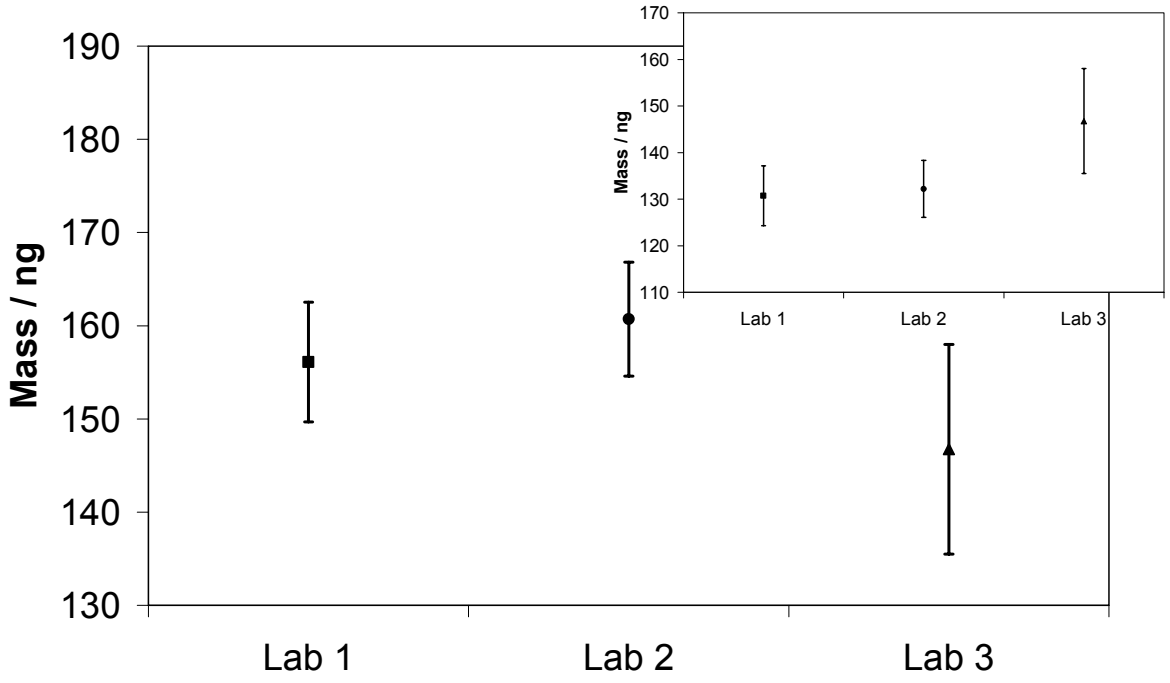


Figure 9. Average mass of nickel measured on filter cuts by the three participating laboratories. The average mass of nickel measured on filter cuts by the three participating laboratories excluding the significant outliers from Lab 1 and Lab 2 is also shown (inset).

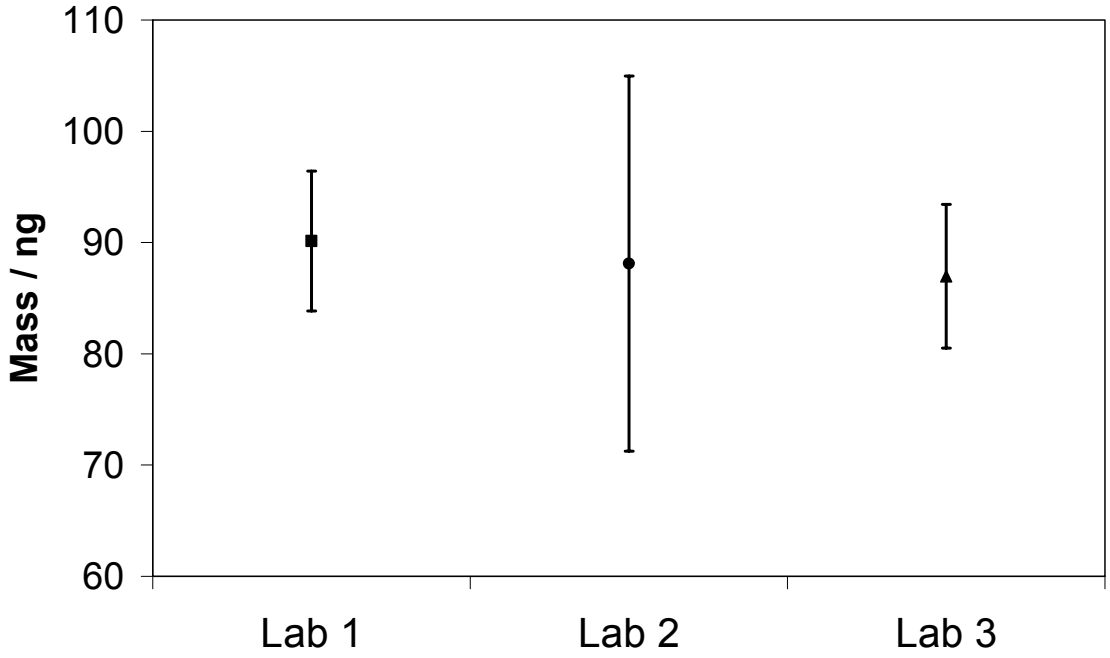


Figure 10. Average mass of arsenic measured on filter cuts by the three participating laboratories.

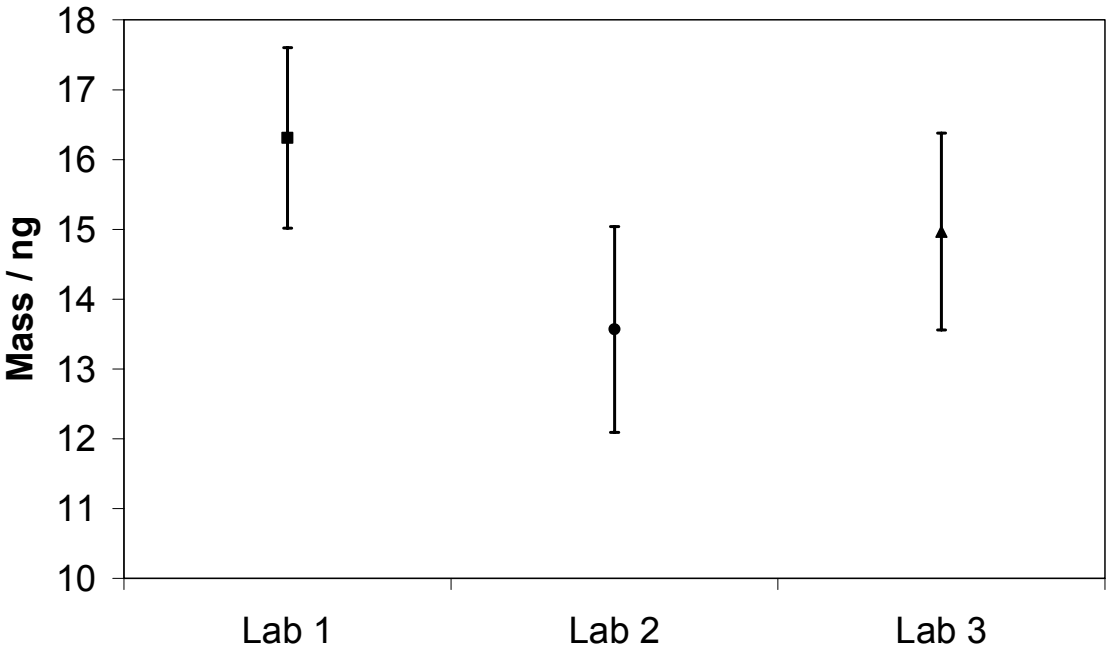


Figure 11. Average mass of cadmium measured on filter cuts by the three participating laboratories.

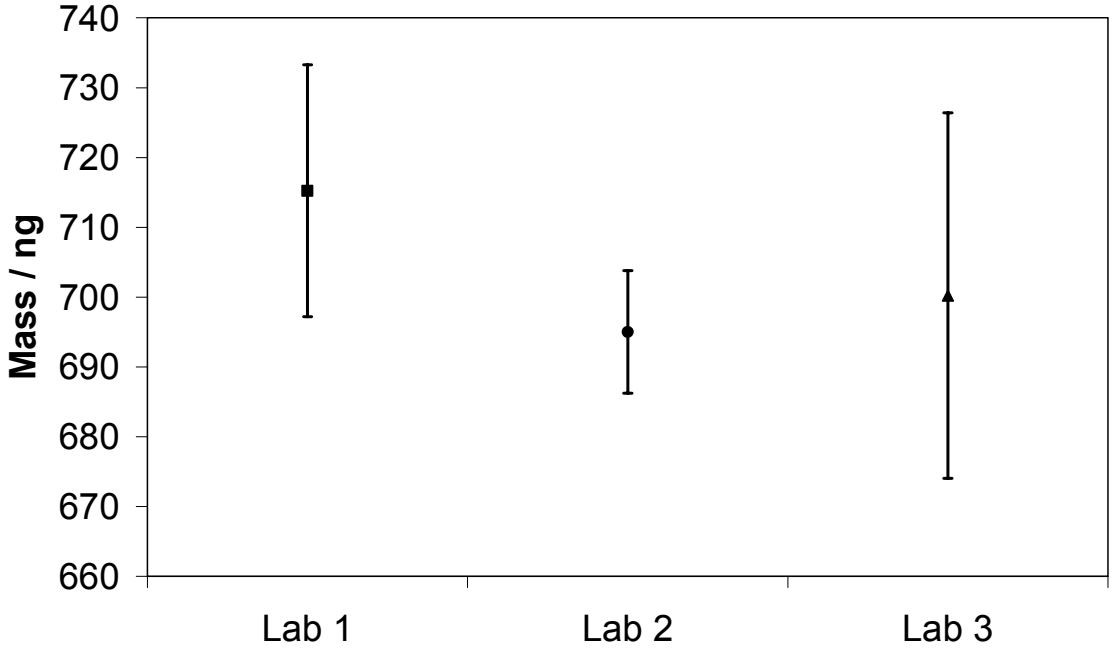


Figure 12. Average mass of lead measured on filter cuts by the three participating laboratories.

These values now show mutual comparability with the possible exception of the cadmium values in Figure 11. However, if an extra uncertainty component, representing the standard deviation of the intra-laboratory values, representative of the uncertainty in recovery, is added in quadrature to the uncertainty of the average laboratory value all values show excellent comparability. An example of the laboratory averaged cadmium values with an expanded uncertainty to include the standard deviation of the intra-laboratory values is shown below in Figure 13.

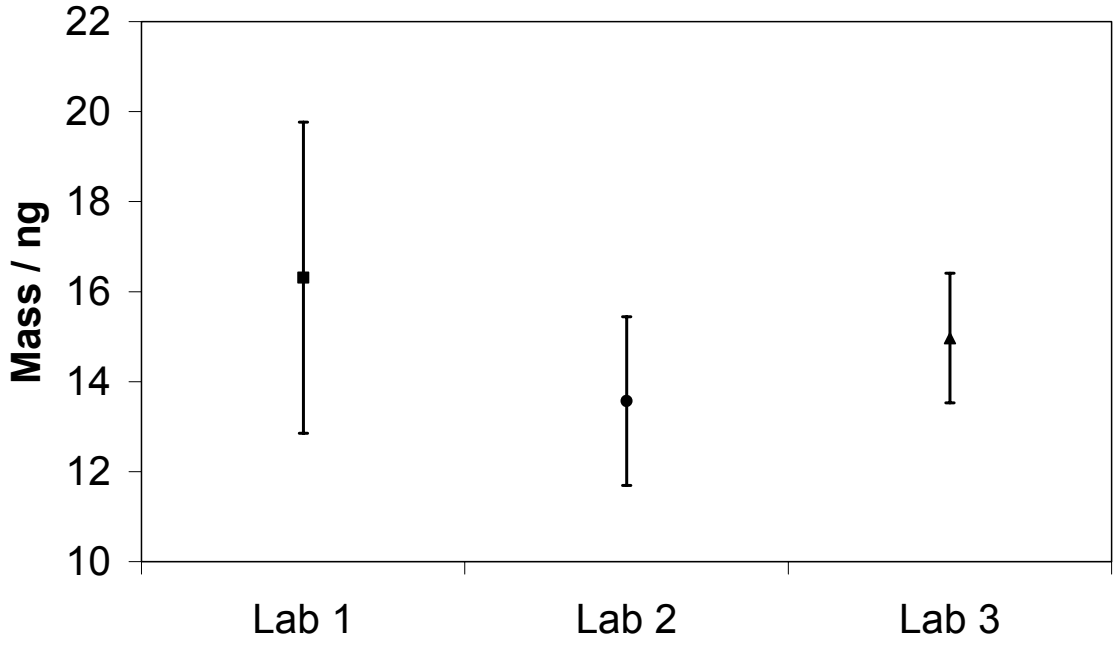


Figure 13. Average mass of cadmium measured on filter cuts by the three participating laboratories including a component owing to intra-laboratory standard deviation within the uncertainty estimate.

Similar plots for the other three analytes are shown Appendix 5. In contrast to the analysis of the NIST SRM 1648 solution the inter-laboratory variability in the analysis of the filter cuts seems to be more random in nature, although some systematic character is still present. For example, filter cut analysis values from Lab 1 have a tendency always to be higher than values from the other two laboratories. Inter-laboratory variability in these values cannot be fully explained by differences in average recovery values reported by the laboratories.

Conclusions

All three laboratories have demonstrated very good comparability both for analysis of a NIST SRM 1648 solution and for the analysis of filter cuts from a large air-sampled filter.

However, slight inter-laboratory systematic biases appear to exist in the analysis of the NIST SRM 1648 solution. A possible explanation for this could be differences in calibration procedures between laboratories.

Inter-laboratory variability in the analysis of the filter cuts is assumed to be caused by both intra-laboratory random, and intra-laboratory systematic, variations in the recovery achieved by each laboratory and also the systematic bias exposed during analysis of the NIST SRM 1648 solution. No correction was made for recovery in the presentation of results since the recovery data submitted by each laboratory were deemed not to differ significantly.

Appendix 1 : Comparison Protocol

Protocol for comparison of the measurement of Ni, As, Cd and Pb contents in ambient air

Background

Three laboratories, NPL (Lab 1), Lab 2 and Lab 3, will participate in this comparison of the measurement of Nickel (Ni), Arsenic (As), Cadmium (Cd) and Lead (Pb) contents, on air-sampled filters and in solutions containing NIST SRM 1648, using one of two different analytical techniques, ICP-MS and GF-AAS.

Preparation by NPL

- NPL will acquire an ambient air sample of the PM_{10} particulate fraction in the Teddington area, during favourable meteorological conditions, using an Andersen GMW High-Volume Sampler calibrated according to the manufacturer's instructions.

- This sample will be collected on a Whatman ashless (Grade 41) filter.

- From this sampled filter, 12 circular filter cuts (44mm diameter) will be taken. **(It is assumed that the inhomogeneity of the sampled material on the filter will not be significant with respect to the uncertainty of the analytical measurement).**

- 12 circular filter cuts (44mm diameter) will also be taken from one un-sampled filter for use in filter blank determinations.

- Filter cuts will be taken using a stainless-steel wad-punch containing negligible content of the metals under examination. These filter cuts will be taken as soon as possible after sampling is complete.

- NPL will additionally prepare an extract of NIST SRM 1648 contained within an aqueous matrix of mass fractions; 11.2% HNO_3, 1.2% H_2O_2. The content of the solution will be unknown to the NPL analyst. All participating laboratories will receive a portion of this solution (along with an indication of the nominal content) for analysis.

- NPL will also prepare an aqueous solution containing mass fractions; 11.2% HNO_3, 1.2% H_2O_2, for use in solution blank determinations.

- Prior to despatch all samples will be kept out of direct sunlight and not exposed to excessive ambient temperatures.

Logistics

- All sampled filter cuts and blank filter cuts will be placed into individual containers as soon as possible after the filter cuts and blank cuts have been taken. Each sample container will be marked with a unique identifying code.

- The pooled NIST SRM 1648 extract solution will be securely packaged in polypropylene sample tubes as soon as possible after preparation. Each sample tube will be marked with a unique identifying code

- **Each laboratory will receive 4 sampled-filter cuts and 4 filter-blank cuts**. All sample and blank sets will be chosen at random from the filter cuts made from the sampled filter and the blank filters. (The filter-blank cuts will be sent in order to allow each laboratory to assess analyte levels in the blank and correct analytical results accordingly).

- **Each laboratory will be asked to analyse 3 of the 4 sampled filter cuts and return the spare one, unopened, to NPL**. This extra filter cut will then be analysed as a quality control standard by NPL to assess whether any significant change in content has occurred during transport.

- **Each laboratory will receive 2 sample tubes containing the NIST SRM 1648 solution and 2 sample tubes containing a solution blank**. Each tube will contain approximately 20 ml of solution.

- **Each laboratory will be asked to analyse the content of 1 of the 2 sample tubes containing the NIST SRM 1648 solution and return the spare one, unopened, to NPL**. This extra sample tube will then be analysed as a quality control standard by NPL to assess whether any significant change in content has occurred during transport

- **Each laboratory is asked to acknowledge safe receipt of samples as soon as possible after delivery by sending a confirmatory e-mail to Richard.Brown@npl.co.uk**

- Each laboratory is asked to store the samples away from direct sunlight and avoid exposing the samples to excessive ambient temperatures.

- Each laboratory will be invited to invoice NPL for usual expenses incurred during the transport and analysis of samples.

- Returned quality control samples should be sent to:

  Dr Richard J. C. Brown
  Centre for Optical and Analytical Metrology
  National Physical Laboratory
  Queens Road
  Teddington
  TW11 0LW
  UNITED KINGDOM

- Serious and obvious logistical failures in the procedures, such as samples being lost or obviously compromised during transit will result in the comparison being declared void, and new samples being prepared by NPL.

Reporting of results

- Each laboratory will be asked to report results and return the quality control samples within a month of receiving the samples.

- Results are to be reported by completion of the comparison results form (see Appendix).

- Results should be sent electronically to Richard.Brown@npl.co.uk

- Results returned for the filter cuts should be stated in nanograms (ng) of nickel, arsenic, cadmium and lead per filter cut. Each result should have an accompanying measurement uncertainty at the 95% confidence level which will encompass the digestion and analytical procedure. **It will be assumed that the filter cut results have been blank corrected unless otherwise stated. It will be assumed that the filter cut results have NOT been corrected for recovery of a CRM unless otherwise stated.**

- **Laboratories will be asked to briefly describe their extraction procedure in the 'comments' section of the reporting sheet.**

- Results returned for the NIST SRM 1648 solution extract should be stated as a mass fraction x 10^9 (parts per billion, ppb) of nickel, arsenic, cadmium and lead in the sample solution. Each result should have an accompanying measurement uncertainty at the 95% confidence level which will encompass analysis step. **It will be assumed that the NIST SRM 1648 solution extract results have been blank corrected unless otherwise stated.**

- **Laboratories may additionally report the levels of analyte in the filter blanks and solution blanks if they wish.**

- Each laboratory is additionally asked to provide data detailing the average recovery of NIST SRM 1648 obtained, using the extraction procedure employed during the comparison, as a percentage of the certified value. Each laboratory is also asked to provide the uncertainty (at the 95% confidence level) of this average recovery value based on variability of the laboratory's repeated recovery of the CRM material. This helps provide a way of more directly assessing comparability between laboratories who do not correct for recovery and those who do. **It is expected that this data will be readily available to all laboratories as a result of experience from previous investigations and will not require extra work as part of the comparison.**

Comparison Outputs

- A short report presenting the results from all participating laboratories and discussing the robustness of the comparison trial will be produced by Dr Richard J. C. Brown (NPL) as soon as possible after the receipt of all results and analysis of the returned quality control samples.

- **After this, each organisation is free to use the results as they wish providing the identities of the participants, apart from their own laboratory, remain anonymous.**

Comparison Results Form

Results reporting sheet for the intercomparison of the measurement of Ni, As, Cd and Pb concentrations in ambient air.

Laboratory name :	
Date of sample receipt:	
Date of sample analysis:	

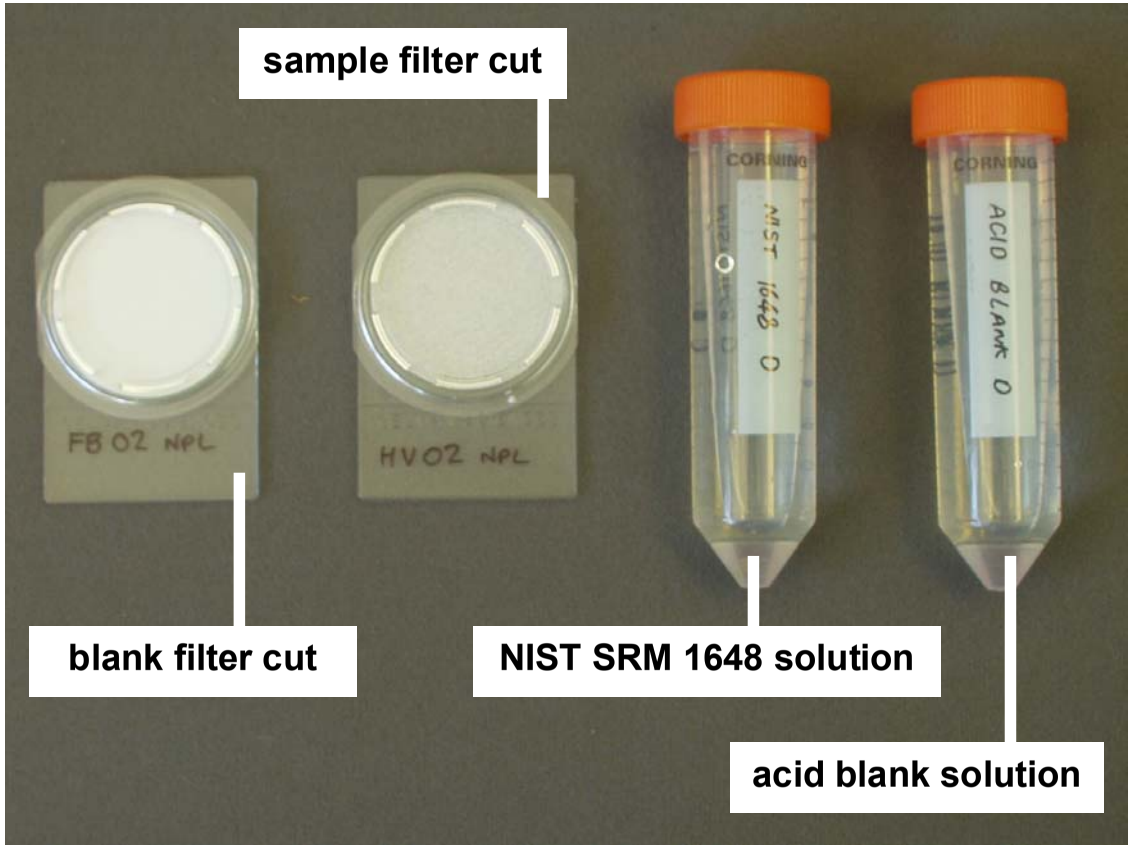
Filter Cut Identifier	Mass of analyte on filter cut with the associated expanded measurement uncertainty at the 95% confidence level							
	Nickel		Arsenic		Cadmium		Lead	
	Mass (ng)	Uncertainty (ng)	Mass (ng)	Uncertainty (ng)	Mass (ng)	Uncertainty (ng)	Mass (ng)	Uncertainty (ng)
Average Filter Blank Value (optional)								

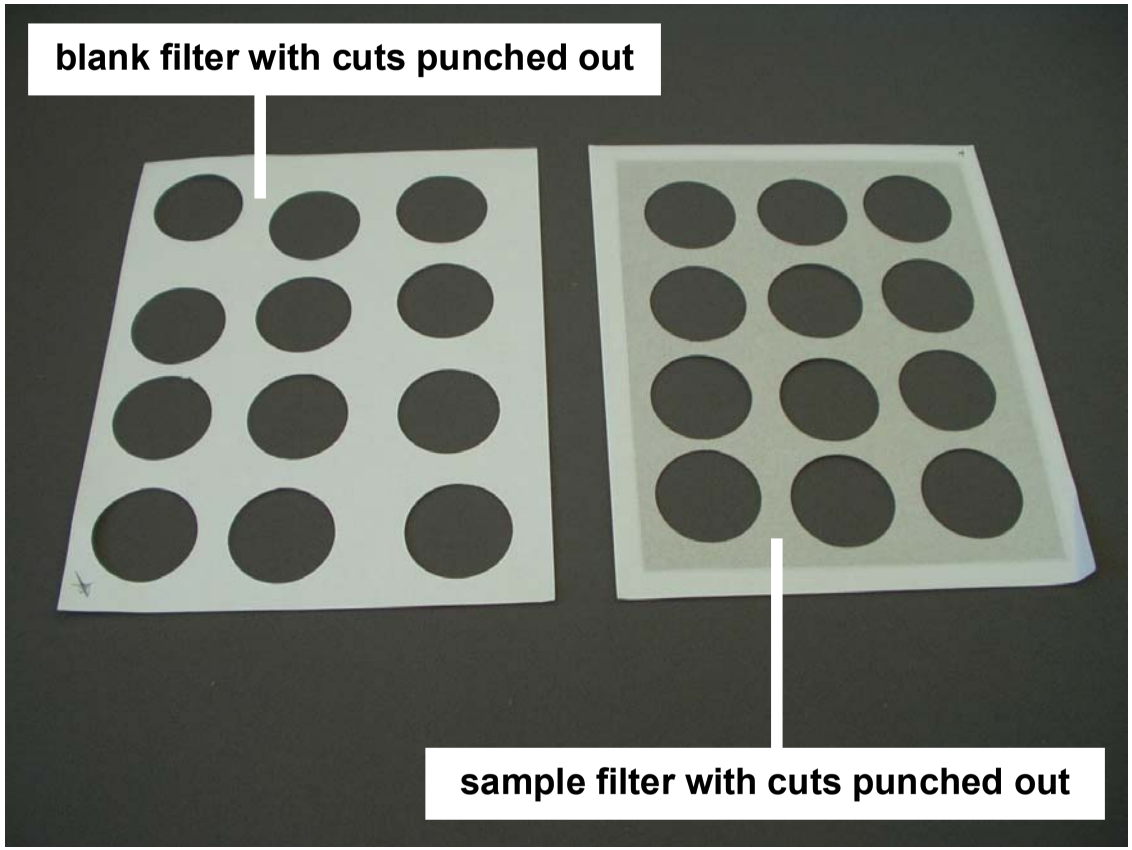
Sample tube identifier	Mass fraction of analyte in the NIST 1648 solution with the associated expanded measurement uncertainty at the 95% confidence level							
	Nickel		Arsenic		Cadmium		Lead	
	Mass fraction (ppb)	Uncertainty (ppb)	Mass fraction (ppb)	Uncertainty (ppb)	Mass fraction (ppb)	Uncertainty (ppb)	Mass fraction (ppb)	Uncertainty (ppb)
Average Solution Blank Value (optional)								

Average recovery of analyte for repeated extractions of NIST 1648 portions, against the certified values, with associated measurement uncertainty at the 95% confidence level							
Nickel		Arsenic		Cadmium		Lead	
Recovery (%)	Uncertainty (% absolute)	Recovery (%)	Uncertainty (% absolute)	Recovery (%)	Uncertainty (% absolute)	Recovery (%)	Uncertainty (% absolute)

Comments:

Appendix 2 : Photographs of Comparison Samples




blank filter with cuts punched out
sample filter with cuts punched out

Appendix 3 : Returned Comparison Results Forms

Results reporting sheet for the intercomparison of the measurement of Ni, As, Cd and Pb concentrations in ambient air.

Laboratory name : National Physical Laboratory
Date of sample receipt: 07/08/03
Date of sample analysis: 19-22/08/0

Filter Cut Identifier	Mass of analyte on filter cut with the associated expanded measurement uncertainty at the 95% confidence level							
	Nickel		Arsenic		Cadmium		Lead	
	Mass (ng)	Uncertainty (ng)	Mass (ng)	Uncertainty (ng)	Mass (ng)	Uncertainty (ng)	Mass (ng)	Uncertainty (ng)
HV04	121.2	10.3	83.36	9.93	12.88	2.11	665.9	30.2
HV06	206.8	12.9	92.72	11.46	19.23	2.46	731.7	32.4
HV11	140.3	9.9	94.33	11.19	16.82	2.12	748.1	31.1
Average Filter Blank Value (optional)	-	-	-	-	-	-	-	-

Sample tube identifier	Mass fraction of analyte in the NIST 1648 solution with the associated expanded measurement uncertainty at the 95% confidence level							
	Nickel		Arsenic		Cadmium		Lead	
	Mass fraction (ppb)	Uncertainty (ppb)	Mass fraction (ppb)	Uncertainty (ppb)	Mass fraction (ppb)	Uncertainty (ppb)	Mass fraction (ppb)	Uncertainty (ppb)
NIST 1648 A	6.49	0.31	9.76	0.45	6.09	0.27	531	21
Average Solution Blank Value (optional)	-	-	-	-	-	-	-	-

Average recovery of analyte for repeated extractions of NIST 1648 portions, against the certified values, with associated measurement uncertainty at the 95% confidence level								
Nickel		Arsenic		Cadmium		Lead		
Recovery (%)	Uncertainty (% absolute)	Recovery (%)	Uncertainty (% absolute)	Recovery (%)	Uncertainty (% absolute)	Recovery (%)	Uncertainty (% absol
87.51	8.16	97.17	9.04	92.87	9.44	91.99	5.14

Comments:
All uncertainties are expressed with a coverage factor k=2.
Average filter blank value and solution blank values are subtracted from sample values before reporting.
Recoveries are given as an average of the recoveries of 5 extractions. The uncertainty in the mean recovery is the standard deviation of the 5 recoveries and the average of the 5 associated uncertainties added in quadrature.
The results given for the sample tube and filter cuts are averages of 2 repeat analyses. The uncertainties are treated as above.
There is an extra component in the uncertainty of the mass of the metals on each filter cut - notably the uncertainty in the total mass of each diluted sampl which has also been added in quadrature.

Results reporting sheet for the intercomparison of the measurement of Ni, As, Cd and Pb concentrations in ambient air.

Laboratory name :
Date of sample receipt: 11-Aug-03
Date of sample analysis: 23-Sep-03

Filter Cut Identifier		Mass of analyte on filter cut with the associated expanded measurement uncertainty at the 95% confidence level											
		Nickel	Cov. Factor = 2.3	Extended	**Arsenic**	Cov. Factor = 2.3	Extended	**Cadmium**	Cov. Factor = 2.3	Extended	**Lead**	Cov. Factor = 2.3	Extended
		Mass (ng)	Uncertainty (ng)	Uncertainty (ng)	Mass (ng)	Uncertainty (ng)	Uncertainty (ng)	Mass (ng)	Uncertainty (ng)	Uncertainty (ng)	Mass (ng)	Uncertainty (ng)	Uncertainty (ng)
	HV09D ng/F	150	4	18	88.9	2.0	11.2	15.4	0.5	2.4	715	13	46
	HV10D ng/F	164	5	21	86.6	2.3	11.2	14.8	0.6	2.5	689	15	47
	HV12D ng/F	153	4	19	88.8	2.4	11.2	15.0	0.5	2.4	700	11	43
Average		156	4	19	87.4	2.2	11.2	15.1	0.5	2.4	702	13	46

Filter Cut Identifier		Mass of analyte on filter cut with the associated expanded measurement uncertainty at the 95% confidence level											
		Nickel	Cov. Factor = 2.3	Extended	**Arsenic**	Cov. Factor = 2.3	Extended	**Cadmium**	Cov. Factor = 2.3	Extended	**Lead**	Cov. Factor = 2.3	Extended
		Mass (ng)	Uncertainty (ng)	Uncertainty (ng)	Mass (ng)	Uncertainty (ng)	Uncertainty (ng)	Mass (ng)	Uncertainty (ng)	Uncertainty (ng)	Mass (ng)	Uncertainty (ng)	Uncertainty (ng)
	FB09D ng/F	15.1	0.7	2.2	0.68	0.31	0.63	0.12	0.16	0.32	1.12	0.27	0.55
	FB10D ng/F	6.0	0.4	1.0	0.31	0.27	0.54	0.08	0.14	0.28	1.14	0.28	0.56
	FB12D ng/F	5.8	0.4	1.1	0.19	0.34	0.67	0.09	0.08	0.12	1.07	0.32	0.64
Average		9.0	0.5	1.4	0.39	0.31	0.61	0.10	0.12	0.24	1.11	0.29	0.58

Sample tube identifier	Mass fraction of											
	Nickel	Cov. Factor = 2.3	Extended Solution	**Arsenic**	Cov. Factor = 2.3	Extended Solution	**Cadmium**	Cov. Factor = 2.3	Extended Solution	**Lead**	Cov. Factor = 2.3	Extended Solution
	Mass (ng)	Uncertainty (ng)	Uncertainty (ng)	Mass (ng)	Uncertainty (ng)	Uncertainty (ng)	Mass (ng)	Uncertainty (ng)	Uncertainty (ng)	Mass (ng)	Uncertainty (ng)	Uncertainty (ng)
NIST F	7.07	0.50	1.00	10.7	0.41	0.82	6.42	0.19	0.38	560	0.1	16.3
Acid Blank F	0.07	0.01	0.02	0.002	0.004	0.009	0.005	0.003	0.007	0.05	0.01	0.02
Average												

Average											
Nickel	Cov. Factor = 4.53	Extended	**Arsenic**	Cov. Factor = 4.53	Extended	**Cadmium**	Cov. Factor = 4.53	Extended	**Lead**	Cov. Factor = 2.65	Extended
Recovery (%)	Uncertainty (% abs.)	Uncertainty (% abs.)	Recovery (%)	Uncertainty (% abs.)	Uncertainty (% abs.)	Recovery (%)	Uncertainty (% abs.)	Uncertainty (% abs.)	Recovery (%)	Uncertainty (% abs.)	Uncertainty (% abs.)
96	**4**	**14**	**104**	**2**	**12**	**95**	**3**	**15**	**102**	**2**	**7**

Comments:

Uncertainty 1. Cov. Factor : standard deviation x coverage factor (2.3, 2.65, 4.53 depending on number of determinations performed)
Uncertainty 2. Extended : 2 x ([(standard deviation x coverage factor)^2 + (100 - recovery rate NIST 1648)^2 + (uncertainty NIST 1648)^2] ^ 1/2)
Uncertainty 3. Extended Solution 2 x Cov. Factor

Attention !! **No blank correction performed for filter cuts nor for NIST solution !!**

Digestion procedure : temperature controlled (CEM Mars 5)
material of digestion vessels : fluorocarbon polymer
volume of digestion vessels : 100 ml
digestion matrix : 8 ml concentrated nitric acid + 2 ml hydrogen peroxide
Digestion programme :

Step	Ramp	Temp	Hold	Power
1	3 min	140°C	3 min	1200 W
2	20 min	220°C	25 min	1200 W
3	cooling			

During ramp time, temperature in the digestion vessels is constantly increased until the preset end temperature of the respective step is reached. Pressure increases to about 25 bar (220 °C). After cooling down to room temperature, the contents of the vessels are transferred into calibrated 100 ml PFA flasks and diluted to 100 ml with ultra-pure deionised water.

Results reporting sheet for the intercomparison of the measurement of Ni, As, Cd and Pb concentrations in ambient air.

Laboratory name :	
Date of sample receipt:	11/08/2003
Date of sample analysis:	20-08-03 (Cd-Pb) - 25/08/03 (Ni) - 27/08/03 (As)

Filter Cut Identifier	Mass of analyte on filter cut with the associated expanded measurement uncertainty at the 95% confidence level							
	Nickel		Arsenic		Cadmium		Lead	
	Mass (ng)	Uncertainty (ng)	Mass (ng)	Uncertainty (ng)	Mass (ng)	Uncertainty (ng)	Mass (ng)	Uncertainty
HV03 A	262	3	80	28	14	2.7	788	11
HV05 A	174	10	79	27	12	2.9	687	18
HV08 A	179	12	79	28	12	1.0	675	9.4
FB05 A	51	13	*-12*	4.2	*-0.8*	0.7	*29*	19
FB07 A	47	4.7	*-11*	19	*-1.1*	1.3	*22*	8.2
FB08 A	35	7.9	*-2.8*	20	*-0.8*	2.5	*14*	7.7

Sample tube identifier	Mass fraction of analyte in the NIST 1648 solution with the associated expanded measurement uncertainty at the 95% confidence level							
	Nickel		Arsenic		Cadmium		Lead	
	Mass fraction (ppb)	Uncertainty (ppb)	Mass fraction (ppb)	Uncertainty (ppb)	Mass fraction (ppb)	Uncertainty (ppb)	Mass fraction (ppb)	Uncertainty
NIST - NPL solution	8.008	0.431	11.44	0.386	6.817	0.211	611.5	45.75
Reagent blank - NPL solution	*0.492*	0.213	*-0.012*	0.944	*0.003*	0.021	*0.418*	0.198

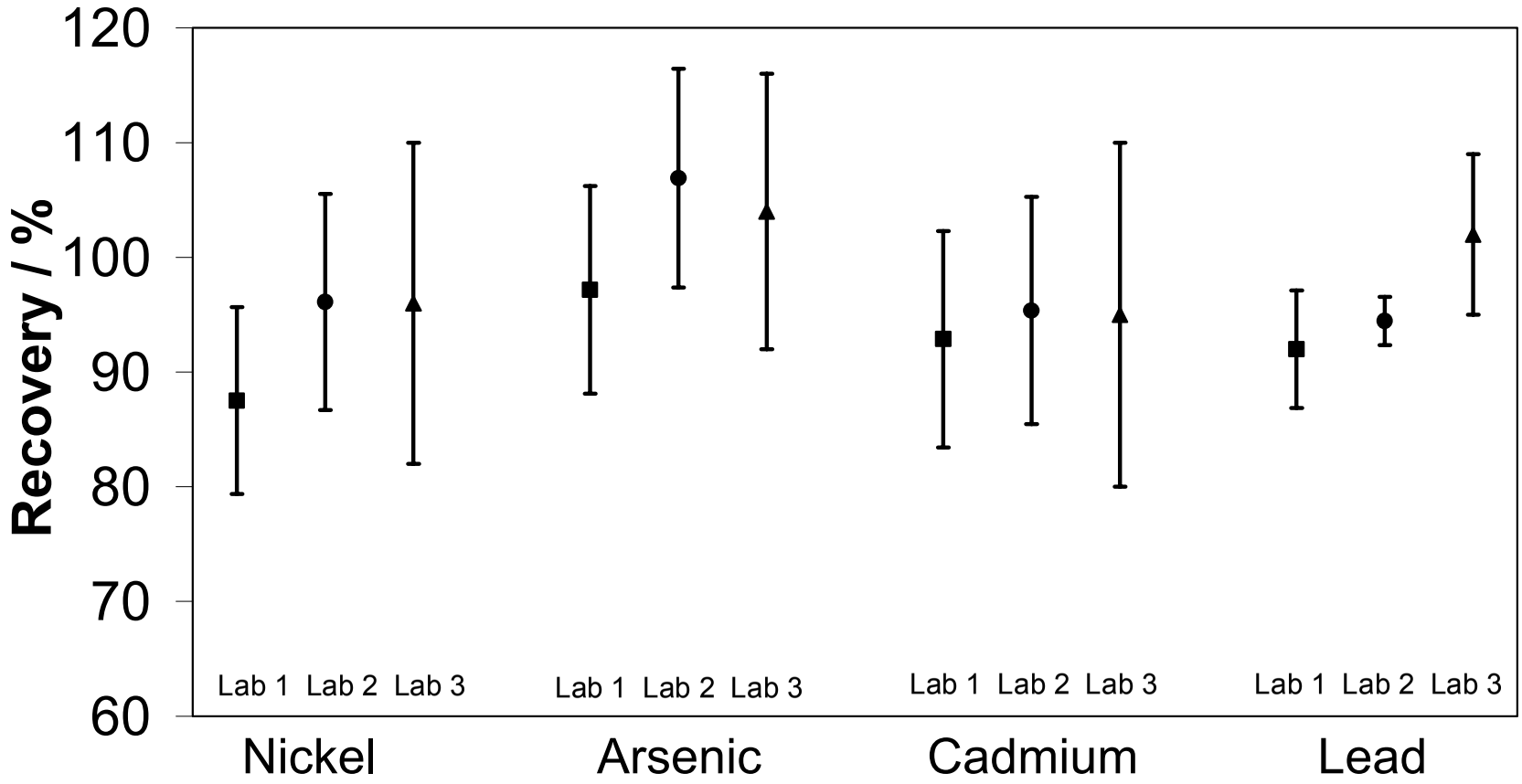
	Average recovery of analyte for repeated extractions of NIST 1648 portions, against the certified values, with associated measurement uncertainty at the 95% confidence level							
	Nickel		Arsenic		Cadmium		Lead	
	Recovery (%)	Uncertainty (% absolute)	Recovery (%)	Uncertainty (% absolute)	Recovery (%)	Uncertainty (% absolute)	Recovery (%)	Uncertainty (%
NIST NPL solution								

Comments: Uncertainty = Standard Deviation * 4.53 (every sample is measured 3 times)
DL: Ni 0,632 µg/l; As 0,468 µg/l; Cd 0,052 µg/l and Pb 0,655 µg/l

	Nickel		Arsenic		Cadmium		Lead	
	Conc	Uncertainty	Conc	Uncertainty	Conc	Uncertainty	Conc	Uncertainty
Additional test: NIST 1648 solution digestion aan analysis	75.10	4.78	121.7	6.7	71.79	1.78	6245	120
	76.44	0.37	124.4	4.3	69.54	3.57	6134	205
	87.23	0.80	122.7	11.3	73.24	1.71	6195	128
Test Blank Value Solution	*0.827*	0.193	*0.084*	0.198	*0.009*	0.016	*0.626*	0.172
	0.543	0.063	*-0.110*	0.144	*-0.001*	0.014	*0.819*	0.425
	0.963	0.138	*-0.067*	0.125	*0.003*	0.014	*0.602*	0.288

Conc in mg/kg for NIST and ppb for reagent blank

Appendix 4 : Recovery of NIST SRM 1648



Appendix 5 : Average masses of nickel, arsenic and lead measured on filter cuts by the three participating laboratories including a component owing to intra-laboratory standard deviation within the uncertainty estimate.