INTERLABORATORY COMPARISON SURVEY OF THE DETERMINATION OF CHROMIUM, MANGANESE, IRON, TITANIUM IN DUST AND ARSENIC, CADMIUM, COBALT AND CHROMIUM IN URINE

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Abstract

This report describes an intercomparison survey based on the Danish External Quality Assessment Scheme (DEQAS). The study was carried out in 1998 for 10 laboratories in a research project on assessment of levels and health effects of airborne particulate matter in mining, metal refining and metal working industries using nuclear and related analytical techniques. The project was co-ordinated by IAEA. Eight laboratories measured chromium (Cr), manganese (Mn), iron (Fe) and titanium (Ti) in welding fume dust loaded on filters. Six laboratories measured arsenic (As), four laboratories measured cadmium (Cd), and five laboratories measured cobalt (Co) and four laboratories measured chromium (Cr) in urine. The target values of the quality control materials were traceable to certified reference materials with respect to Cr in welding fume and As, Cd, Co and Cr in urine. For Mn, Fe and Ti in welding fume the target values were established based on values from reference laboratories and consensus values from several DEQAS rounds. For evaluating the analytical performance the z-score and E_n number were calculated as recommended in ISO 45. The judgement of laboratories according to the performance scores revealed that few laboratories could maintain an ideal z-score below 3 and an ideal E_n number below 1.

Nearly all participants had a high precision in the reported results. This is a good basis for improvements. The deviations from the target values appear to be systematic, because the deviations for Mn, Fe, Ti in welding dust as well as for As, Cd, Co and Cr in urine were a linear function of the target values (ISO 5725 evaluation). The cause for this bias is unknown at present and might not be the same for all participants. It is necessary to look further into the cause for this bias. Therefore, validation of the methodologies and regularly use of certified reference materials are highly recommended.

1. INTRODUCTION

Assessment of levels and health effects of airborne particulate matters at the workplace requires a spectrum of actions. These include monitoring of workplace r for potential chemical hazards in order to assess and reduce exposure. A complementary method is the examination of blood and urine specimens of the individual worker in biological monitoring programmes. For the measurement data to be sound and reliable they must be obtained under a good quality assurance system including internal and external quality control [1,2]. The global acceptance of the *Guide to expression of uncertainty in measurement* (GUM) has attracted attention to the need for controlling measurement results [3,4]. In order to achieve this objective it is recommended to report the uncertainty of measurement results, and whenever possible, to participate in External Quality assessment Schemes (EQAS).

Various terms may be used to describe schemes for external quality assessment, e.g., external quality control, performance schemes, interlaboratory comparison, proficiency testing, etc. Although there are several types of schemes, they all share the common feature of comparison of a laboratory's results with those of other laboratories. EQAS are used to

determine the performance of individual laboratories for specific measurements, and to monitor the continuing performance of laboratories described by laboratory bias, stability, repeatability and traceability as described in ISO 5725 [5-7].

EQAS can be extremely valuable if they are designed properly, taken the uncertainty of measurement results into account, and in addition taken seriously by the participating laboratories. Commonly used statistics for quantitative results in EQAS are the deviation of the participants result from the assigned (target) value, and z-score, which is the difference between the participants results and the assigned value divided by an estimate of variability. A value of $|z| \leq 3$ is satisfactory [8]. ISO 43 recommends that to calculate E_n numbers, which is the difference between the participants result and the assigned value divided by the squared sum of the uncertainty of the participants result and the uncertainty of the assigned value. A value of $|E_n| < 1$ is satisfactory [8,9].

The Danish external quality assessment scheme (DEQAS) is developed and managed by the National Institute of Occupational Health (Arbejdsmiljøinstituttet, AMI) in Denmark. It is designed to evaluate the quality of results of measurements of a group of laboratories. The scheme, which evaluates performance at different concentrations of the component, is used to evaluate laboratories in the field of occupational health. Currently, DEQAS comprises proficiency testing schemes for lead and manganese in blood, iron, manganese and titanium in welding fumes (dust), and organic solvents on charcoal tubes [10,11]. However, this paper will present the results of an intercomparison survey on chromium, iron, manganese, and titanium in welding fumes loaded on filters, and arsenic, cadmium, cobalt and chromium in urine. The participants in this IAEA-DEQAS are the contractors of the IAEA co-ordinated research project on "Assessment of levels and health effects of airborne particulate matters in mining, metal refining and metal working industries using nuclear and related analytical techniques".

2. METHODS

2.1. Danish external quality assessment scheme

The Danish EQAS is designed to ensure a homogenous quality of workplace measurements. The individual laboratory is evaluated on the basis of reference values (target values) or consensus values calculated on the basis of all observations obtained after statistical rejection of outliers. In the present project the participating laboratories received one sample for analysis of Cr in welding dust, three samples for analysis of Mn, Fe and Ti in welding dust, and three samples for analysis of As, Cd, Co and Cr in urine. The target values were at three different concentrations. Each laboratory received sheets for reporting the results and the analytical techniques.

2.2. Quality control samples and distribution

The preparation of the filters loaded with welding dust for analysis of chromium, manganese, iron and titanium has previously been described [11,12]. Filters (borosilicate microfibre glass discs without resin binder) loaded with Cr (VI) for determination of chromium in welding dust were weighed before and after the loading with welding fume dust originating from a manual metal arc computerised welding system. The amount of dust loaded on the filter was known for each filter and was 2.585, 2.786, 2.300, 2.455, 2.500, 2.578, 1.634, 2.659 mg for the filters B1-52, B1-53, B1-63, B1-64, B1-66, B1-71, B1-72, B1-91, respectively. The chromium concentration in the control material is traceable to the Community Bureau of Reference BCR certified reference material CRM 545.

The urine was obtained from normal healthy donors. Samples at three different concentrations were produced, low level (baseline level), medium level (spiking of standard solution) and high level (spiking of standard solution), respectively. Spiking solutions were prepared using dimethylarsinic acid (SIGMA C 0250, 98 % pure), Cd atomic absorption standard solution (SIGMA C 5524, 1000 μg Cd/L), Cr atomic absorption standard solution (SIGMA C 5899, 1005 μg Cr/L) and Co atomic absorption standard solution (SIGMA C 7405, 970 μg Co/L). The materials were spiked as described in Table I.

TABLE I. TARGET VALUES AND SPIKING AMOUNTS FOR AS, CO, CD AND CR IN LOW, MEDIUM AND HIGH QUALITY CONTROL MATERIALS. VALUES IN BRACKETS ARE EXPECTED ENDOGENOUS CONCENTRATIONS.

Quality control material	**Arsenic**		**Cobalt**		**Cadmium**		**Chromium**	
	Target μg As/L	Spike μg As/L	Target μg Co/L	Spike μg Co/L	Target μg Cd/L	Spike μg Cd/L	Target μg Cr/L	Spike μg Cr/L
Low	(25)	0	(1)	0	(0.5)	0	(1.3)	0
Medium	50	50	10	10	5	5	5	5
High	150	150	60	60	10	10	20	20

Each vial contained 10 ml of lyophilised urine, homogenous and easy to reconstitute in 10.00 ml purified water. The target values of the urine materials are traceable to the Community Bureau of Reference (BCR), draft certified reference material CRM 640, 641, 642 [13]. The samples were delivered to IAEA, Vienna, which distributed the materials to each laboratory.

2.3. Participants

The samples for Cr, Mn, Fe, Ti in welding fume dust were analysed by 8 laboratories, and samples for As, Cd, Co and Cr in urine were analysed by 6, 4, 5 and 4 laboratories, respectively. The participating laboratories are listed in the acknowledgement, and the analytical techniques used by the laboratories are described in Annex 1.

2.4. Statistical model

The main theory is based on the assumption that the analytical method should be in statistical control for all concentrations during the period of analysis, i.e., the results of independent measurements of samples with the same reference value μ are approximately normally distributed (Gaussian distribution). Both the mean value μ_i of the measured metal concentration $E(Y \mid \mu)$ and the experimental standard deviation σ_i may be a function of μ. The bias of the analytical method is defined by $\delta_i = E(Y \mid \mu) - \mu$. Kolomogorov-Smirnov test for goodness of fit to the normal distribution is carried out and Cochran and Grubbs outlier tests are used to identify and exclude outliers [14].

2.5. Target values

The target values were established as target values obtained in certification intercomparison studies (Cr in welding fumes dust, As, Cd, Co and Cr in urine) [13-15]. Consensus mean values, which are the mean values of the results of several DEQAS rounds after outliers exclusion and results obtained by reference laboratories, were established for Mn, Fe and Ti in welding fume dust.

2.6. The method evaluation function

The analytical results were evaluated in relation to the target values. Estimates of the experimental standard deviation of the method used by the laboratories, the slope (β) and the intercept (α) of the regression line were obtained by statistical evaluation (least square regression analysis) of the linear relationship between the results obtained by the laboratory and the target values [6,7]. The ideal method evaluation function (MEF) is given by the intercept (α) and the slope (β) equal to 0.0 and 1.0, respectively [10,16].

2.7. Calculation of the performance statistics

Commonly used performance statistics are the percentage deviation from the target value, the relative standard deviation and the z-score. $Z = (x-X)/s$, where x is the participants result, X is the target value, and s is the standard uncertainty of the target value. Values of $|z| > 3$ may with great confidence be considered due to poor performance. E_n numbers are used in measurement intercomparison schemes, i.e. $E_n = |(x-X)| / (U_{lab}^2 + U_{ref}^2)^{½}$, U_{lab} is the uncertainty of a participant's results and U_{ref} is the uncertainty of the target value established by reference laboratories. Values of $E_n < 1$ is satisfactory [8]. In this report the values of E_n numbers and z-scores are reported with +/- sign.

3. RESULTS AND DISCUSSION

3.1. Chromium in welding dust loaded on filters

The participants were requested to report two results for each sample. Table II (Annex 2), Figures 1 and 2 are from the evaluation report. Figure 1 displays a bar-plot of the obtained values and the uncertainties. The lines indicate the target value and the uncertainty of the target value, 2 and 3 standard deviations, respectively. Figure 2 displays the calculated z-scores from all the laboratories. Lab. 55 and Lab. 58 reported acceptable results.

3.2. Manganese, iron and titanium in welding fumes loaded on filters

The participants were requested to report two results for each filter at three different concentration levels. Table III (Annex 2), Figures 3 and 4 are results from the evaluation report. Figure 3 displays a bar-plot of the obtained values for manganese at low level and the uncertainties. The lines in Figure 3 indicate the target value and the uncertainty of the target value, 2 and 3 standard deviations, respectively. Lab. 53, 54, 56, 58, 59 and 60 reported acceptable results confirmed in Figure 4, displaying the z-scores. Lab. 53, 54, 56, 58, 59 and 60 obtained acceptable $|z|$-scores ≤ 3, at low, medium and high levels of manganese.

Table IV (Annex 2), Figures 5 and 6 are results from the evaluation report. Figure 5 displays a bar-plot of the obtained values for iron and the uncertainties. The lines in Figure 5 indicate target value and the uncertainty of the target value, 2 and 3 standard deviations, respectively. Lab. 53, 54, 56, and 59 show acceptable results as confirmed in Figure 6, illustrating the calculated z-scores from all the laboratories. Lab. 53, 54, 56, 59 and 60 has acceptable $|z|$-scores ≤ 3, at low, medium and high levels of iron.

Table V (Annex 2), Figures 7 and 8 are results from the evaluation report. Figure 5 displays a bar-plot of the obtained values for titanium and the uncertainties. The lines in Figure 7 indicate the target value and the uncertainty of the target value, 2 and 3 standard deviations, respectively. Lab. 53, 55, 56 and 59 reported acceptable results as confirmed in Figure 6, illustrating the calculated z-scores from all the laboratories. Lab. 53, 55, 59 and 60 obtained acceptable scores $|z|$-scores ≤ 3, at low, medium and high levels of titanium.

The ISO 5725 evaluation (regression lines) for all laboratories is presented in Annex 3, Figure 9. Lab. 60 demonstrated excellent performance for Mn, Fe and Ti in welding dust. The regression lines for selected laboratories are shown in Figure 10, 11 and 12. The three laboratories 55, 57 and 58 reported clearly anomalous results and titanium results from Lab. 58 were excluded before the statistical analysis of the results. In Figure 10 the plots for Lab. 59 illustrate that good performance exists for manganese and iron, while the results indicate an analytical bias for titanium. For Lab. 55 the results reveal a poor performance for manganese (analytical bias), but reasonable results for iron and manganese. Lab. 56 demonstrates an excellent performance for manganese and iron, while the analytical method seems to be out of control for titanium, as only titanium results at low level are acceptable.

The results indicate that several of the laboratories may have calibration errors, because most the obtained results show a linear functional relationship.

3.3. Arsenic, cadmium, cobalt and chromium in urine

The participants were requested to report two results for urine samples at three different concentration levels. Table VI (Annex 2), Figures 13 and 14 are results of arsenic in urine from the evaluation report. Figure 13 displays a bar-plot of the obtained values for arsenic at low level, and the uncertainties. The lines in Figure 13 indicate the target value and the uncertainty of the target value, 2 and 3 standard deviations, respectively. From Table VI it is shown that Labs. 53 (low level), 56 (high level) 57 (high level) and 59 (medium and high levels) have acceptable results, confirmed in Figure 14 displaying the calculated z-scores from all the laboratories. Only Lab. 53 obtained acceptable $|z|$-scores ≤ 3 at low level of arsenic. At high level Lab. 56, 57 and 59 have acceptable results ($|z|$-score 1, 2, 1 respectively).

Table VII (Annex 2), Figures 15 and 16 are results of cadmium in urine from the evaluation report. Figure 15 displays a bar-plot of the obtained values for cadmium at medium level and the uncertainties. The lines in Figure 15 indicate the target value and the uncertainty of the target value, 2 and 3 standard deviations, respectively.

None of the laboratories reported acceptable results for all three levels and that is confirmed for cadmium at medium level as illustrated in Figure 16, displaying the calculated z-scores for all the laboratories.

Table VIII (Annex 2), Figures 17 and 18 are results of cobalt in urine from the evaluation report. Figure 17 displays a bar-plot of the obtained values for cobalt at high level and the uncertainties. The lines in Figure 17 indicate the target value and the uncertainty of the target value, 2 and 3 standard deviations, respectively. Only Lab. 59 reported acceptable results at all three levels. The performance is illustrated for cobalt at high level (61.70 µg/L) in Figure 18, displaying the calculated z-scores for all the laboratories.

Table IX (Annex 2), Figures 19 and 20 are results of chromium in urine from the evaluation report. Figure 19 displays a bar-plot of the obtained values for chromium at high level and the uncertainties. The lines in Figure 19 indicate the target value and the standard uncertainty of the target value, 2 and 3 standard deviations, respectively. At the three levels only Lab. 59 reported acceptable analytical performance, as shown for chromium at high level (20.95 µg/L) in Figure 20.

The ISO 5725 evaluation of As and Cd in urine (regression lines, Figure 21) for all laboratories is presented in Annex 3, and the regression lines for selected laboratories are shown in Figure 22, 23 and 24. The laboratories 56 and 57 reported clearly anomalous results. However, chromium results from Lab. 59 were acceptable at medium and high levels. In

Figure 22 the plots for Lab. 53 illustrate that bad performance exists for arsenic and cadmium. For Lab. 58 the result reveals problems with the performance for cadmium, and analytical bias for arsenic in urine as illustrated in Figure 23.

The results indicate that the laboratories maybe have contamination or calibration errors because all of the obtained results at the three concentration levels show a linear functional relationship.

4. CONCLUSION

Eight laboratories reported results for chromium in welding fume dust loaded on filters. Observations deviating as much as 76 % from the target values were seen for a single laboratory. Two laboratories had acceptable performance scores for Cr in welding dust.

Seven laboratories reported results for manganese, iron and titanium in welding fume dust loaded on filters. Observations deviating as much as 479 % from the target value were seen for titanium, but in general the results for manganese and iron were acceptable.

Six laboratories reported results for arsenic in urine, four laboratories reported results for cadmium, and five laboratories reported results for cobalt and four reported results for chromium in urine. For cobalt and chromium in urine only one of the laboratories reported results of acceptable analytical performance.

The judgement of laboratories according to the performance scores showed that few laboratories could maintain an ideal $|z|$-score below 3 and an ideal $|E_n|$ number below 1.

Nearly all participants had a high precision in the reported results. This is a good basis for improvements. The deviations from the target values appear to be systematic, because the deviations were a linear function of the target value (ISO 5725 evaluation). The cause for he bias is unknown at present and might not be the same for all participants.

Some participants reported accurate results in other matrices. One possible cause, therefore, may be matrix effects unknown to the laboratories. Matrices effects can be coped with by method evaluation and be controlled by using certified reference materials. It is necessary to look further into the causes for the systematic deviations.

Validation of the methodologies and regularly use of certified reference materials are highly recommended.

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- Department of Nuclear Analysis, Institute of High Energy Physics, Beijing, China.
- Supervisao de Reator Radioanalise, Centro de Desenvolvimento da Tecnologia Nucl., Belo Horizonte, Minas Gerais, Brazil.
- Environmental Radiological Laboratory, Indian Rare Earths Limited, Udyogamandal, Kerala State, India.

- Institute for Nuclear Science, College of Engineering, University of Nairobi, Kenya
- Physics Department, Nuclear and Technological Institute, Estrada Nacional, Sacavem, Portugal.
- Department of Activation Analysis and Radiation Research, Frank Laboratory of Neutron Physics, Joint Inst. for Nuclear Research, Dubna, Moscow Region, Russian Federation.
- Laboratory for Radiochemistry, Department of Environmental Sciences, Institut Jozef Stefan, Ljubljana, Slovenia.

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SUMMARY OF THE ANALYTICAL TECHNIQUES USED IN THE INTERCOMPARISON COMPARISON STUDY

Fe and Cr were determined by scanning X-ray Fluorescence Spectrometry (XRF). Mn and Ti were determined by short-term neutron activation analysis (NAA) (reported not to be in good condition). No sample preparation and no correction for matrix effects were performed. As, Cd, Cr, and Co were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) without any pre-treatment. In order to avoid missing values in the statistical analysis results below the limit of detection are presented as the limit of detection divided by two (Lab. 53).

Instrumental NAA was used for the determination of Mn, Cr, Fe, Ti in welding fumes. Radiochemical NAA for As and Co in urine (Lab. 54).

XRF was used for determination of Fe, Mn and Ti. Standard samples were obtained from IAEA. ICP-AES was used for quantification of Cr (VI). The filter was dissolved in conc. HNO_3. The organic matter was destroyed by HNO_3–$HClO_4$ mixture and dissolved in 1 M HNO_3. Inductively coupled plasma mass spectrometry (ICP-MS) was used for the determination of Cd in urine. Internal standard was Rh/Ru. Samples were destroyed in 10 ml distilled water and evaporated to dryness. Afterwards the material was treated with 5 ml HNO_3 and 1 ml $HClO_4$. The residue was dissolved in 1M HCl (Lab. 55).

Proton induced x-ray emission (PIXE) technique was used for quantification of elements without any sample pre-treatment. The concentration was obtained in mg/cm^3 for the filter samples and results were calculated to mg/Kg dust for Cr and μg/filter for Ti, Mn and Fe, respectively. The urine samples were reconstituted and lyophilised. There were problems with the freeze-dryer. The recovered material was too small to obtain enough sub-sample for analyses (Lab. 56).

Energy dispersive x-ray fluorescence spectrometry without any pre-treatment of filters was used for the determination of Cr, Mn, Fe and Ti in welding fumes dust on filters. For analysis of As, Cr and Co in urine about 0.1 g of the lyophilised urine materials were weighed and dissolved in 1 ml nickel standard solution. The instrumental equipment used for quantification was total reflection x-ray fluorescence spectrometry (Lab. 57).

Sample preparation was not carried out for determination of Fe, Ti, Mn, and Cr. The instrumental technique was vacuum sequential x-ray spectrometry. All urine samples were determined by flow injection atomic absorption spectrometry (FAAS). As in urine was determined by FAAS with hydride generation. Cd was determined using on-line FAAS with pre-concentration. Urine samples were dissolved in conc. HNO_3/$HClO_4$ heated and dissolved in 2M HNO_3 (Lab. 58).

Instrumental NAA was used for determination of elements on filters, which were palletised with a manual press. Filters for Cr (VI) determination were dissolved in conc. HNO_3 and analysed by atomic absorption spectrometry (AAS). As alternative technique energy dispersive X-ray fluorescence spectrometry was performed directly on the filters. For Cd determination in urine instrumental NAA and total XRF were used, but the results show that this technique is not sufficiently sensitive for such samples. Urine results were reported in μg/g dry material and then calculated to μg/L urine (Lab.59).

Instrumental NAA were used for determination of Mn, Ti, Cr and Fe. Radiochemical NAA was not applied. None sample pre-treatment was performed except for heat-sealing into polyethylene irradiation vials prior to irradiation (Lab. 60).

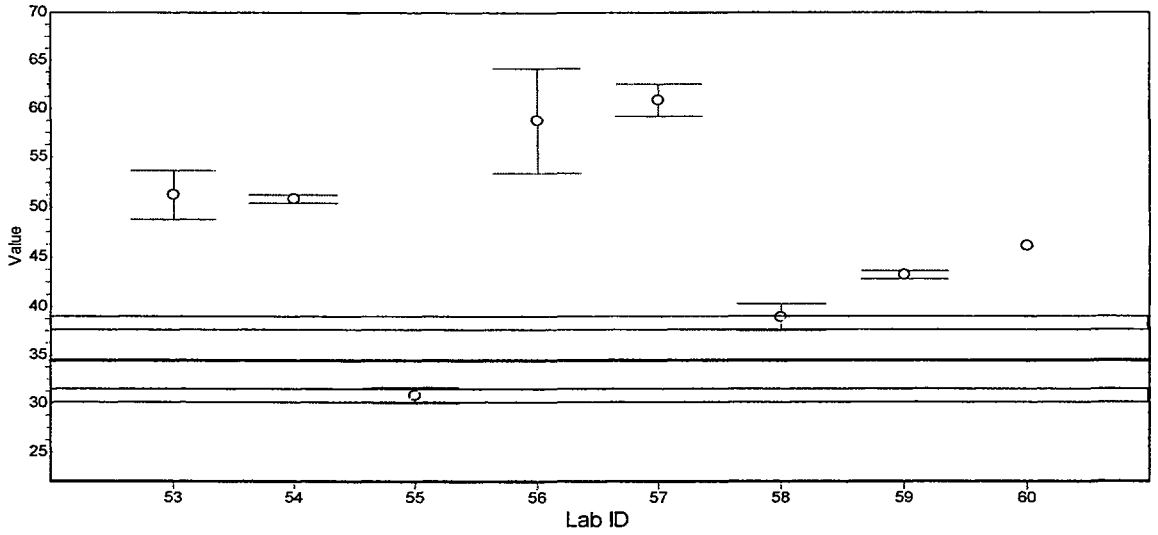


Figure 1. Bar-plot of the obtained values of Cr. Values is in mg/kg dust. The lines indicate the uncertainty of the target value, 2 and 3 standard deviations, respectively.

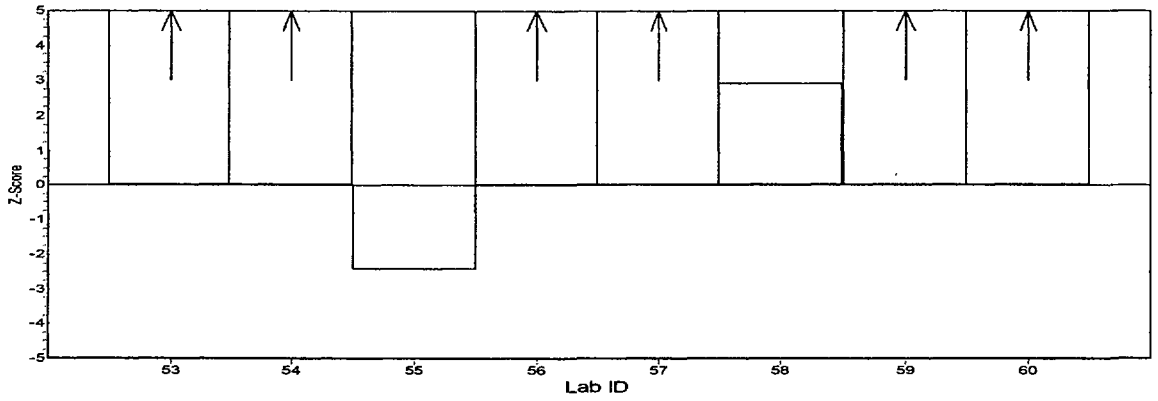


Figure 2. Plot of z-scores for Cr in welding dust. /Z/-scores > 5 indicated by an arrow.

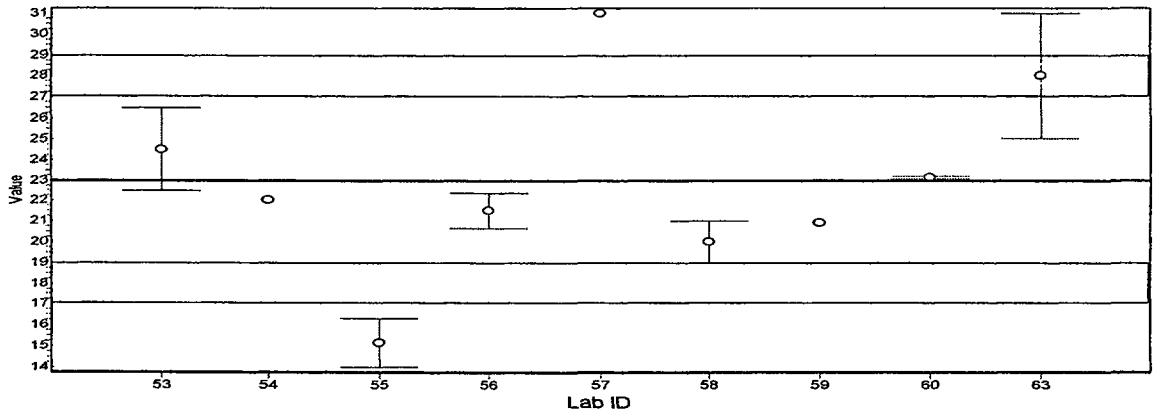


Figure 3. Bar-plot of the obtained values of Mn in welding fume dust. Values in µg/filter.

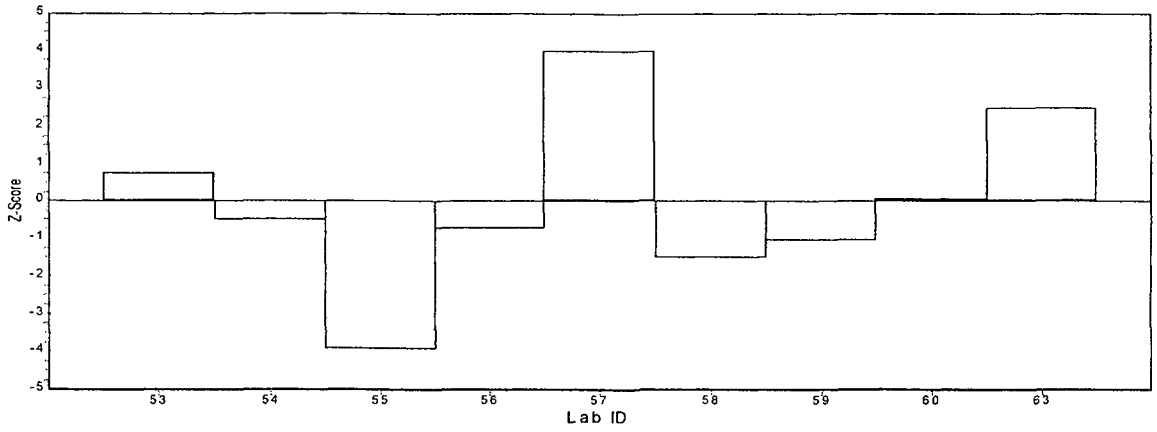


Figure 4. Plot of z-scores for Mn in welding fume dust calculated for all laboratories

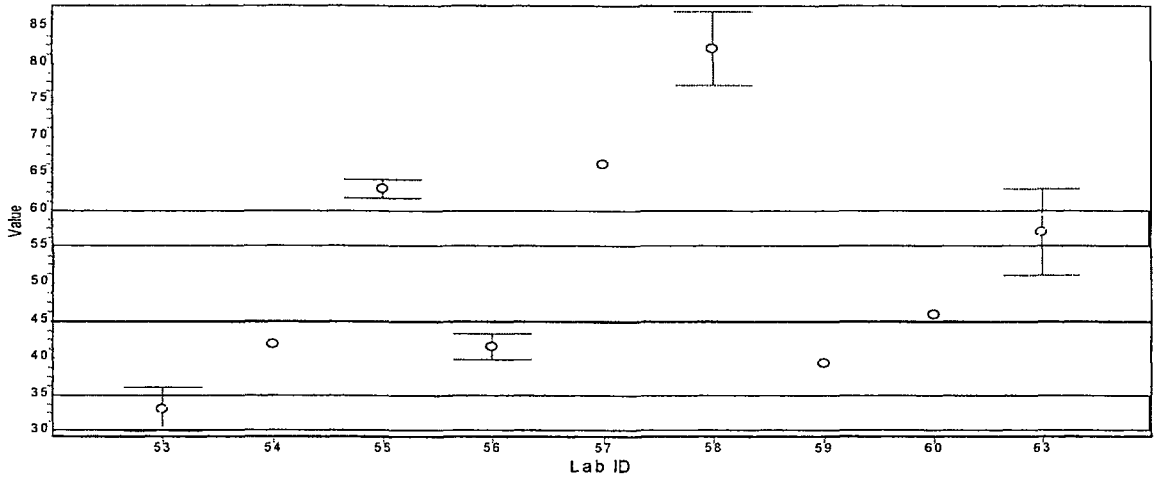


Figure 5. Bar-plot of the obtained values of iron in welding fume dust. Values in µg/filter.

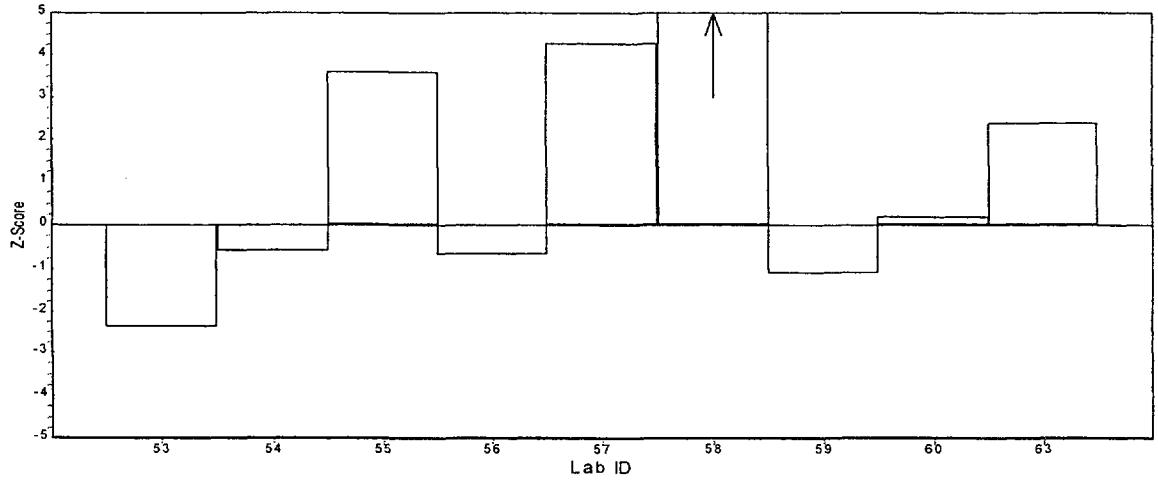


Figure 6. Plot of z-scores for iron in welding fume dust calculated for all laboratories. | Z |-scores > 5 are indicated by an arrow.

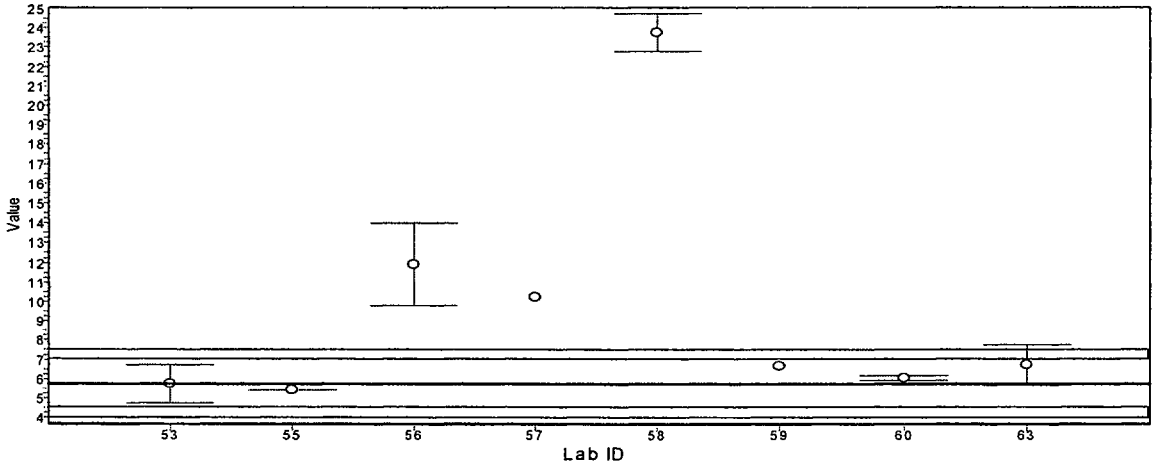


Figure 7. Bar-plot of the obtained values of Ti in welding fume dust. Values in µg/filter.

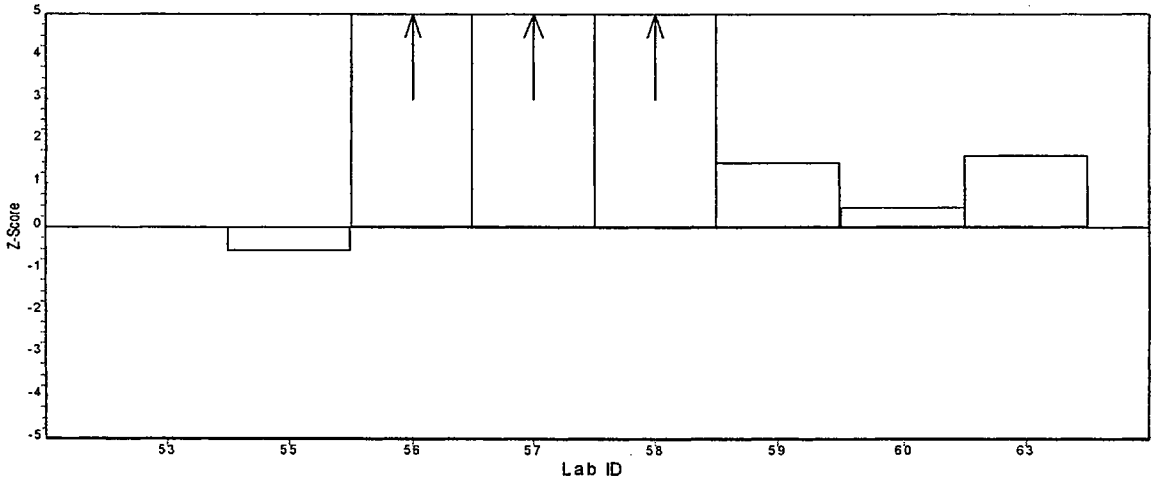


Figure 8. Plot of z-scores for Ti in welding fume dust calculated for all laboratories. /Z/-scores > 5 are indicated by an arrow.

Figure 9. Manganese, iron and titanium in welding fume dust loaded on filters. Results of measurement results obtained by all laboratories.

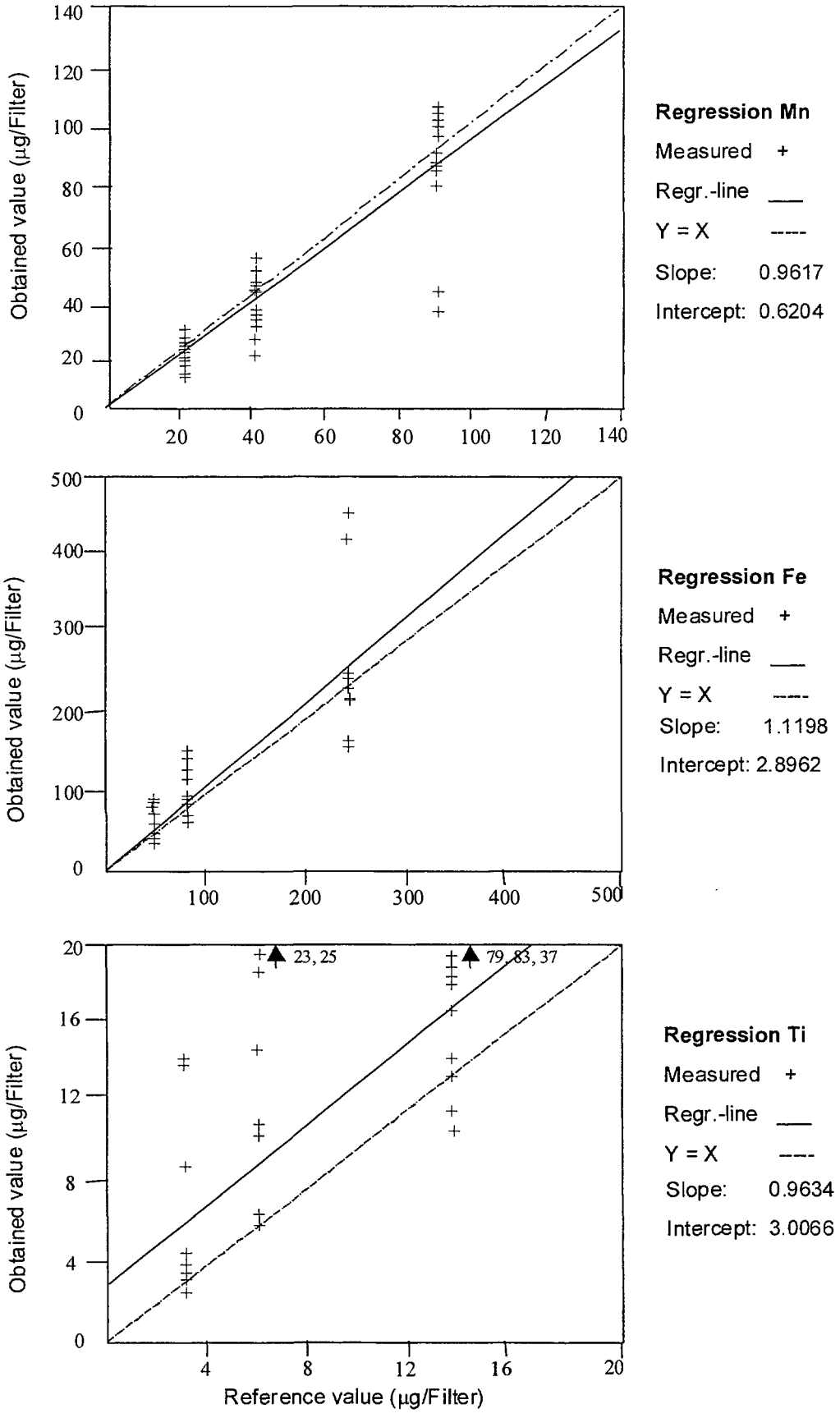
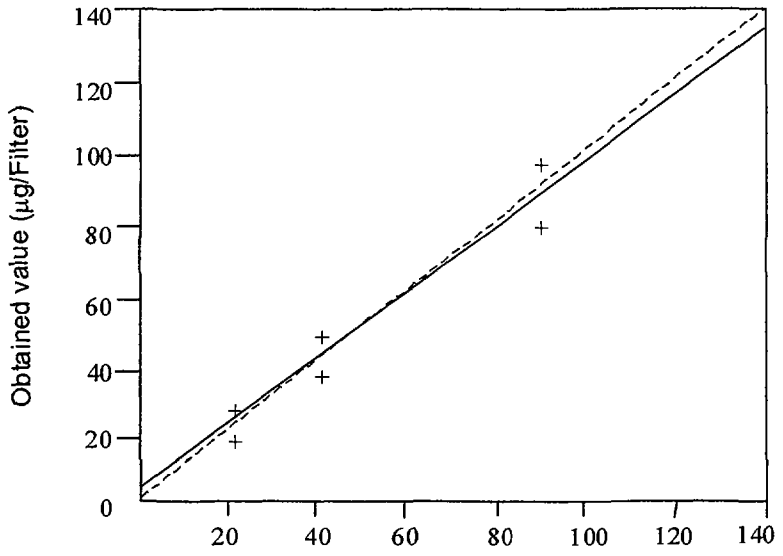


Figure 10. Manganese, iron and titanium in welding fume dust loaded on filters. Results of measurement obtained by laboratory 59.



Regression lab 59 Mn

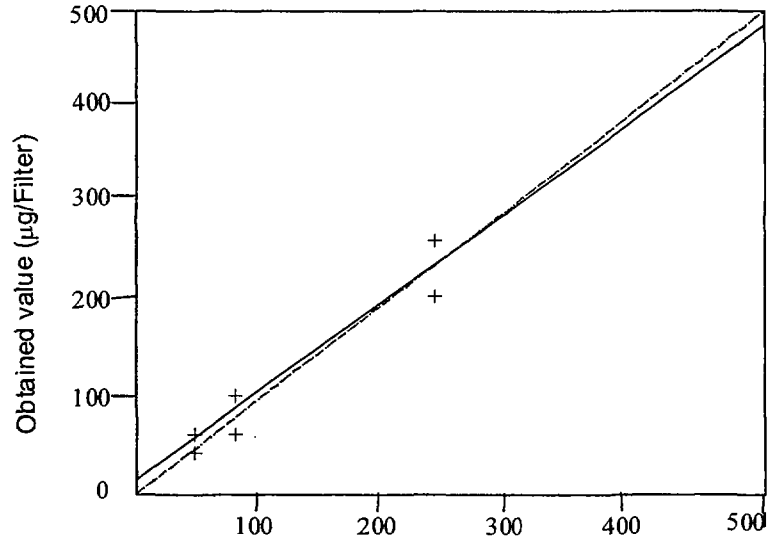
Measured +

Regr.-line ____

Y = X ----

Slope: 0.9495

Intercept: 2.7220



Regression lab 59 Fe

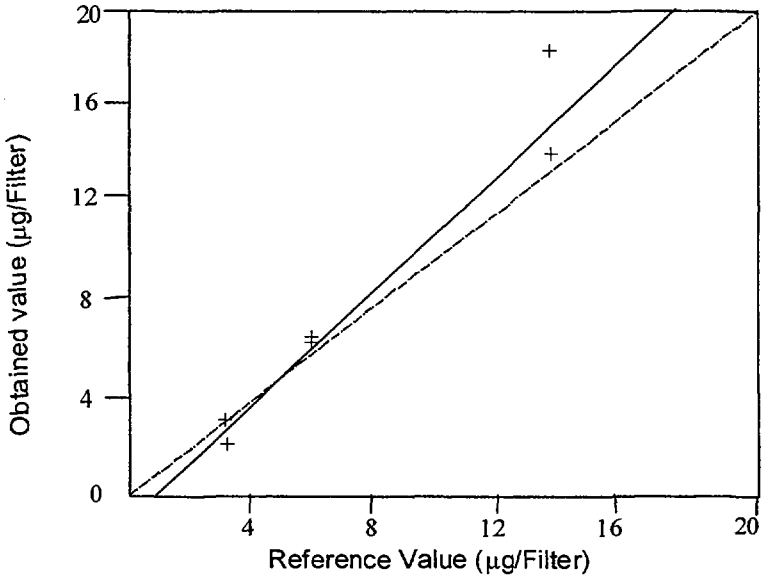
Measured +

Regr.-line ____

Y = X ----

Slope: 0.9619

Intercept: 4.9151



Regression lab 59 Ti

Measured +

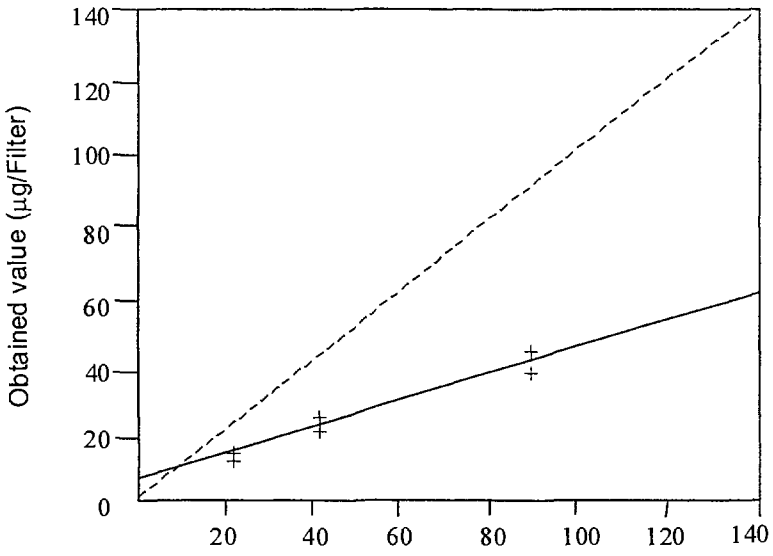
Regr.-line ____

Y = X ----

Slope: 1.3146

Intercept: -1.3642

Figure 11. Manganese, iron and titanium in welding fume dust loaded on filters. Results of measurement obtained by laboratory 55.



Regression lab 55 Mn

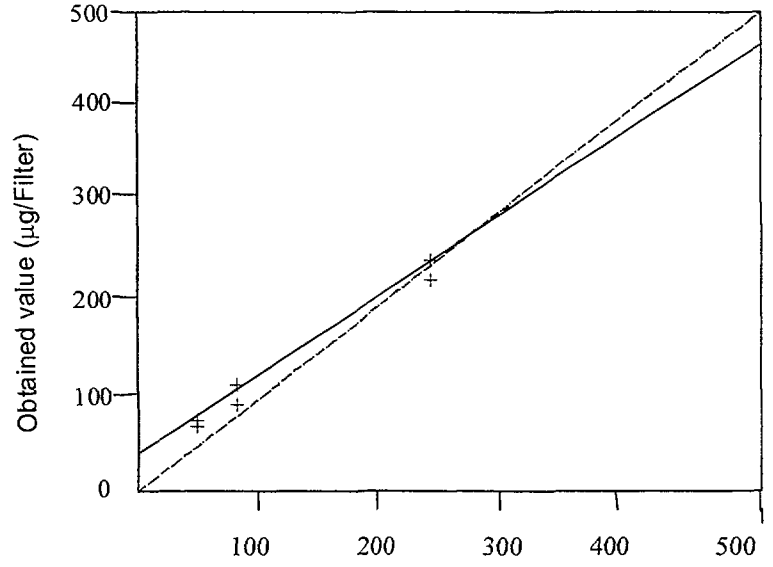
Measured +

Regr.-line ____

Y = X ----

Slope: 0.4049

Intercept: 5.6897



Regression lab 55 Fe

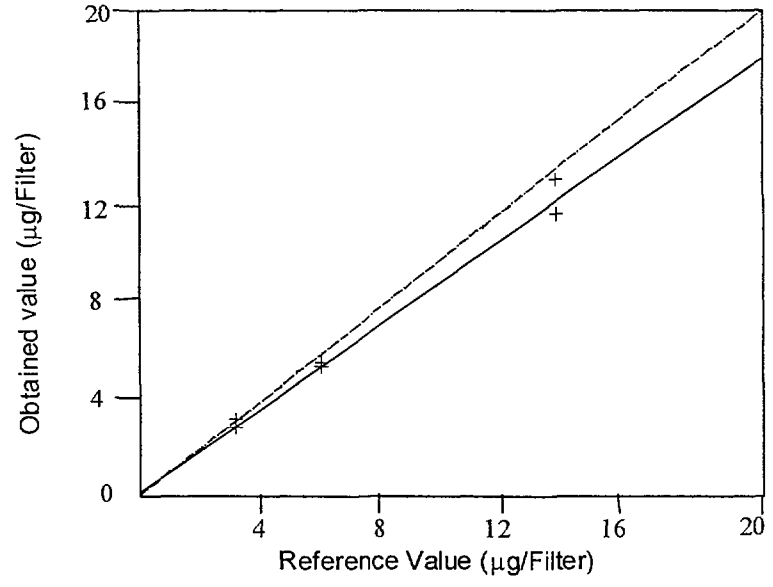
Measured +

Regr.-line ____

Y = X -----

Slope: 0.8994

Intercept: 22.4268



Regression lab 55 Ti

Measured +

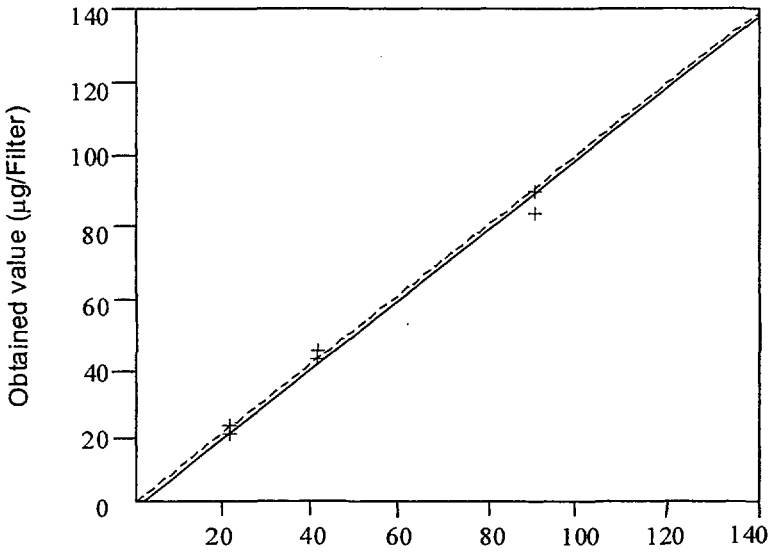
Regr.-line ____

Y = X -----

Slope: 0.8921

Intercept: 0.2216

Figure 12. Manganese, iron and titanium in welding fume dust loaded on filters. Result of measurement results obtained by laboratory 56.



Regression lab 56 Mn

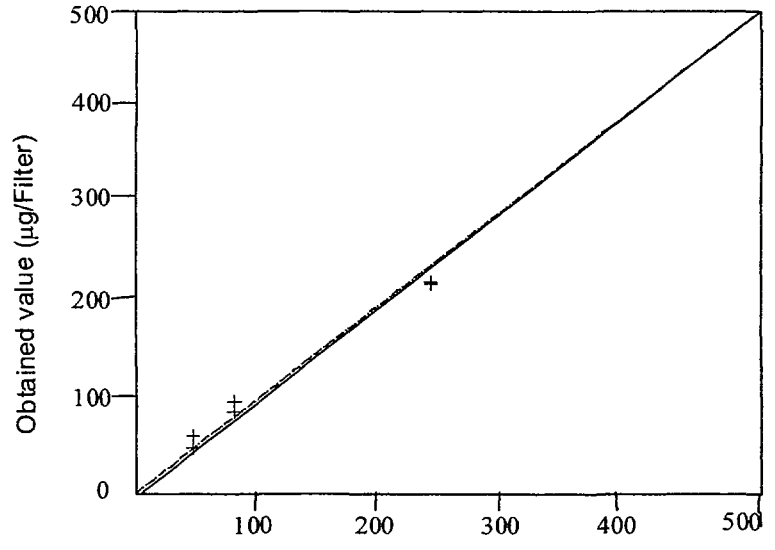
Measured +

Regr.-line ____

Y = X ----

Slope: 1.0007

Intercept: -1.5034



Regression lab 56 Fe

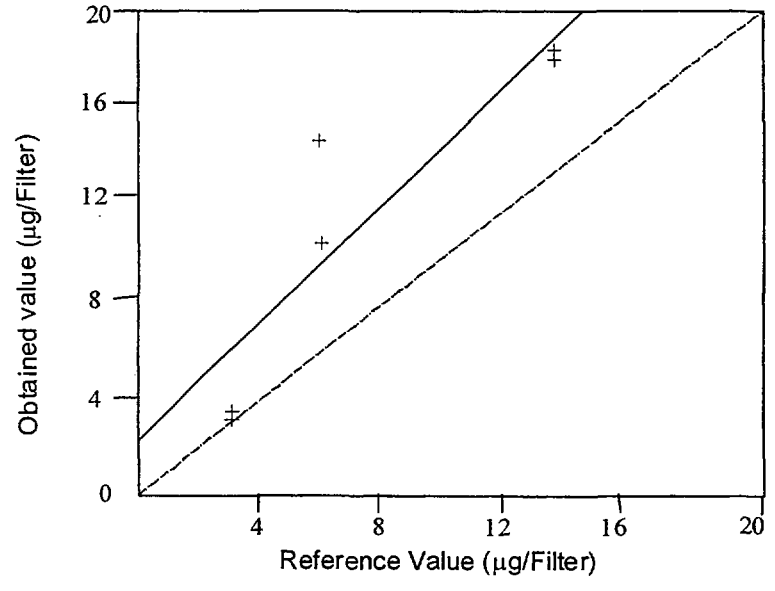
Measured +

Regr.-line ____

Y = X -----

Slope: 1.0101

Intercept: -3.8341



Regression lab 56 Ti

Measured +

Regr.-line ____

Y = X -----

Slope: 1.1582

Intercept: 2.5228

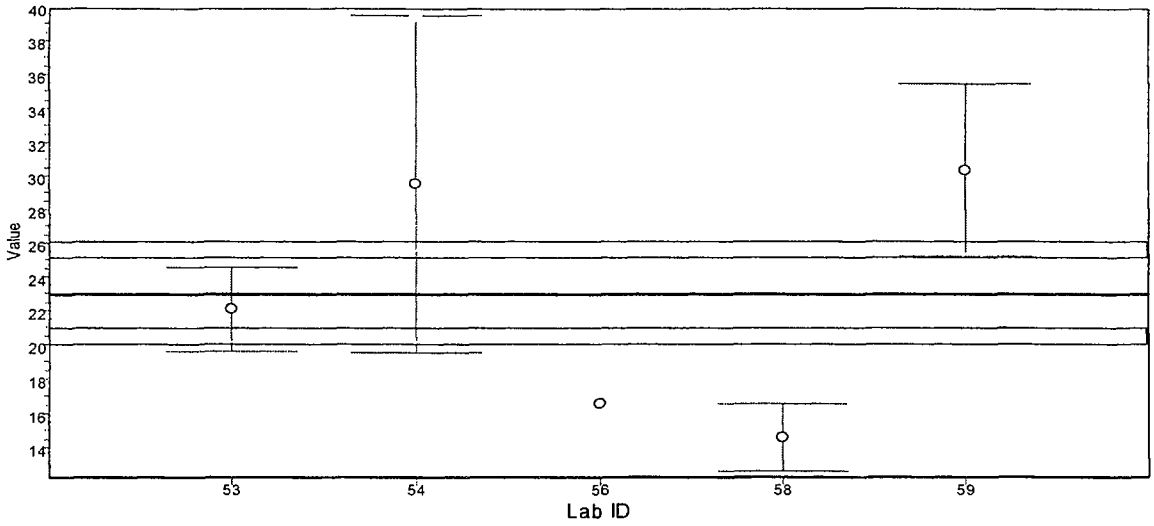


Figure 13. Bar-plot of the obtained values of As in urine (μg/L) at target value 23.45 μg/L.

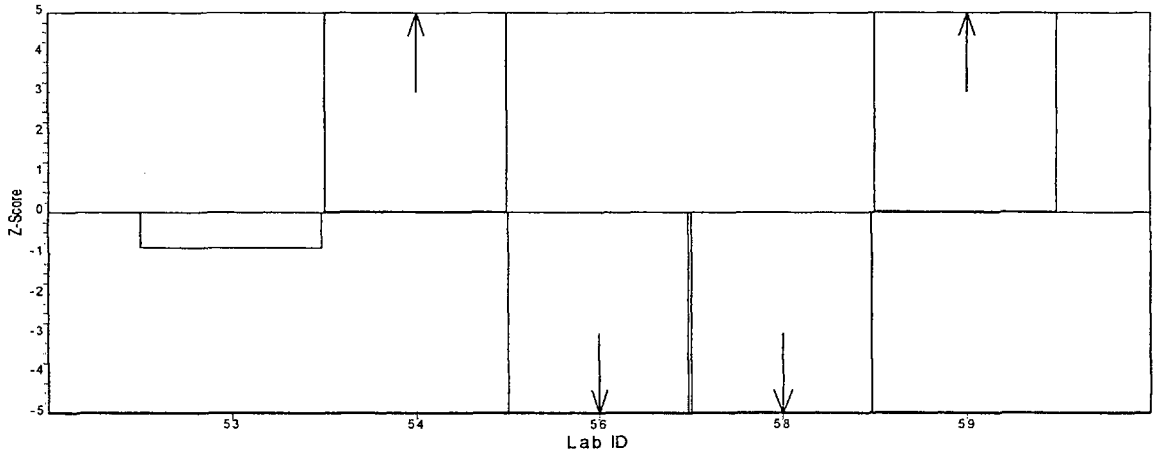


Figure 14. Plot of z-scores for As in urine calculated for all laboratories at target value 23.45 μg/L. |Z|-scores > 5 are indicated by an arrow.

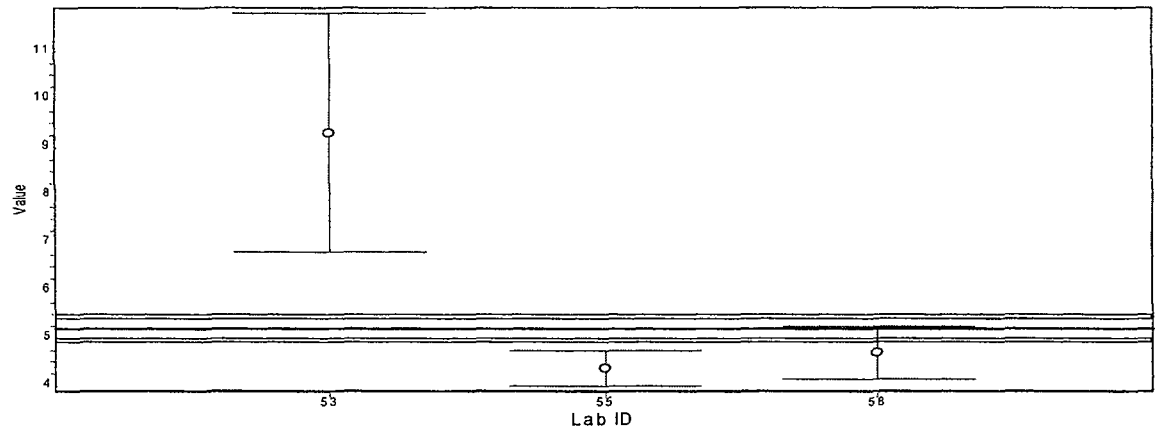


Figure 15. Bar-plot of the obtained values of Cd in urine (μg/L) at target value 5.20 μg/L.

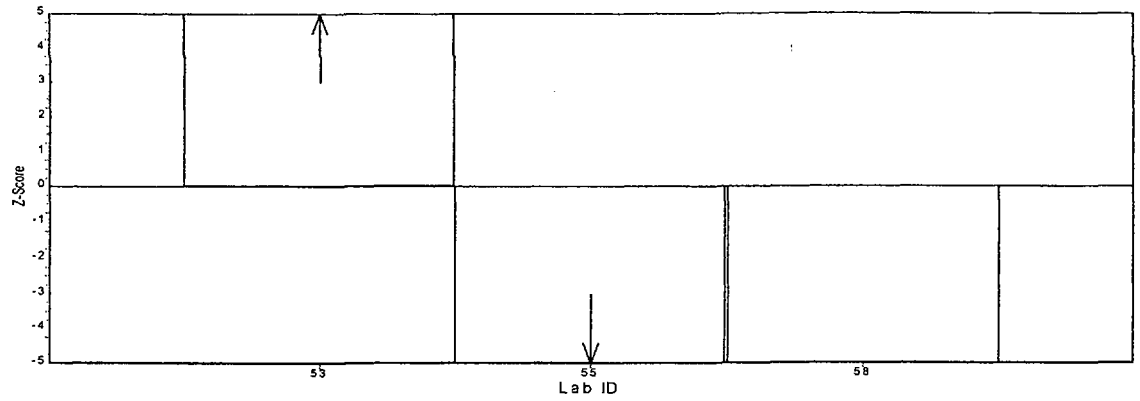


Figure 16. Plot of z-scores of Cd in urine calculated for all laboratories at target value 5.20 µg/L. /Z/-scores > 5 are indicated by an arrow.

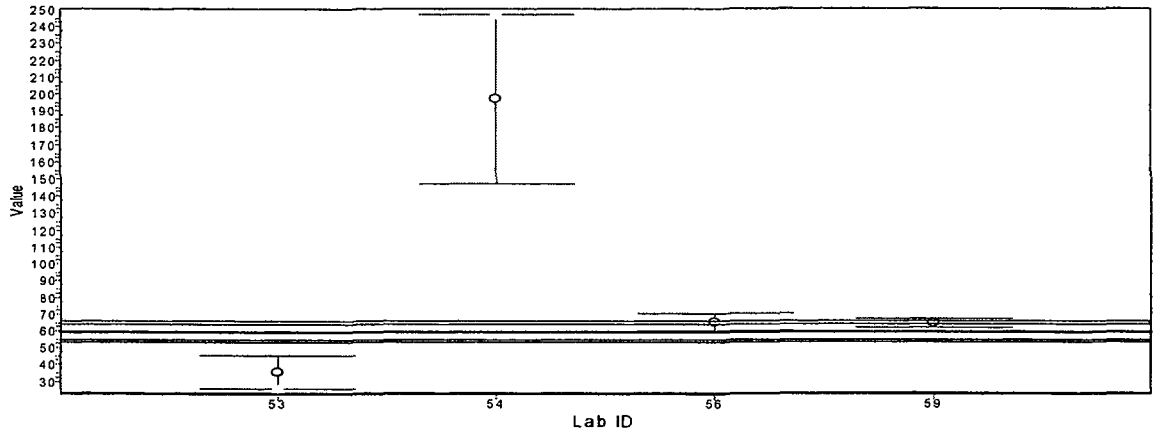


Figure 17. Bar-plot of the obtained values of Co in urine (µg/L) at target value 61.70 µg/L.

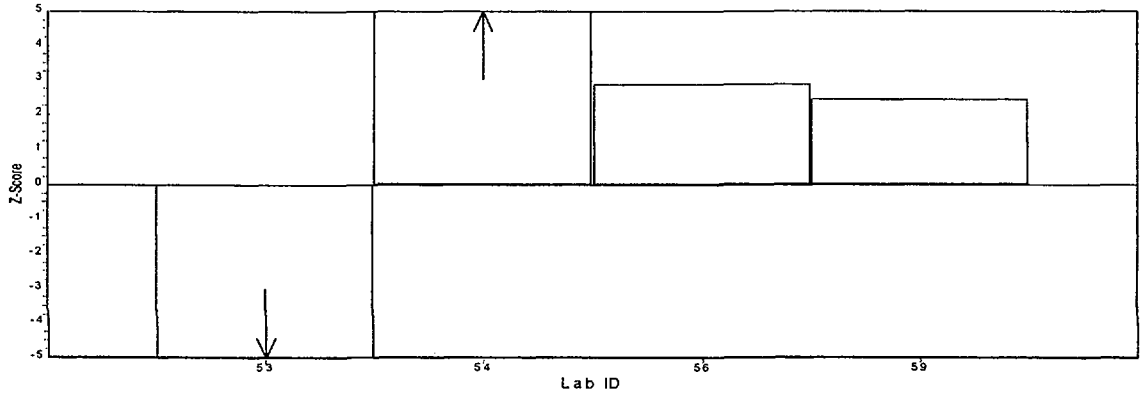


Figure 18. Plot of z-scores of Co in urine calculated for all laboratories at target value 61.70 µg/L. /Z/-scores > 5 are indicated by an arrow.

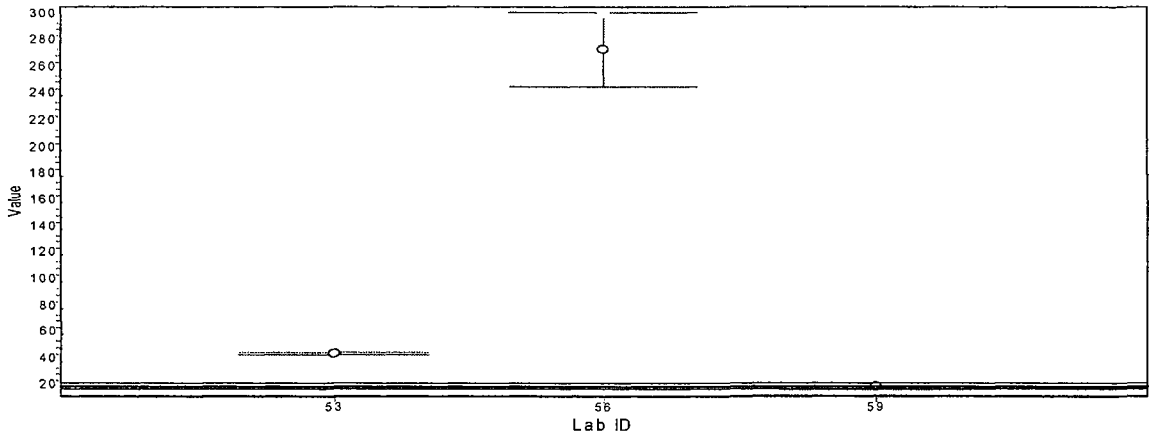


Figure 19. Bar-plot of the obtained values of Cr in urine (µg/L) at target value 20.95 µg/L.

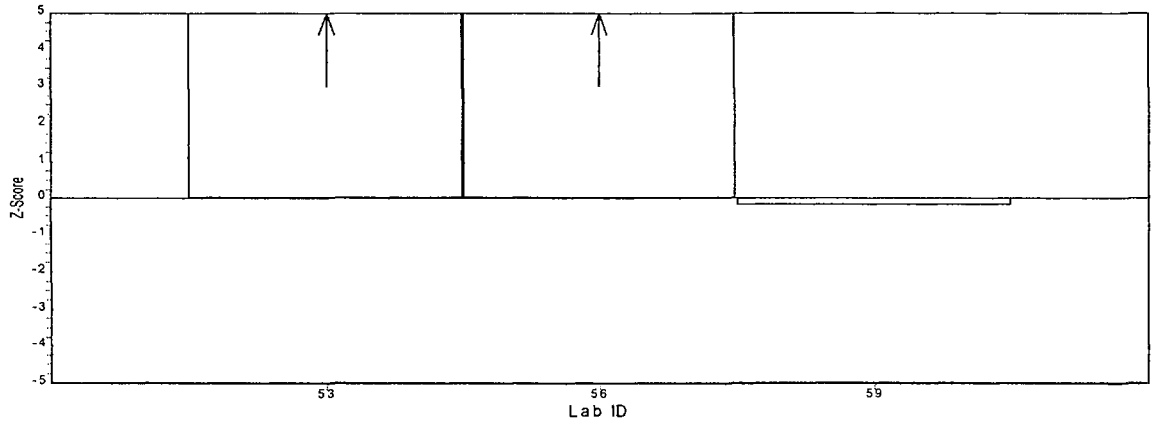
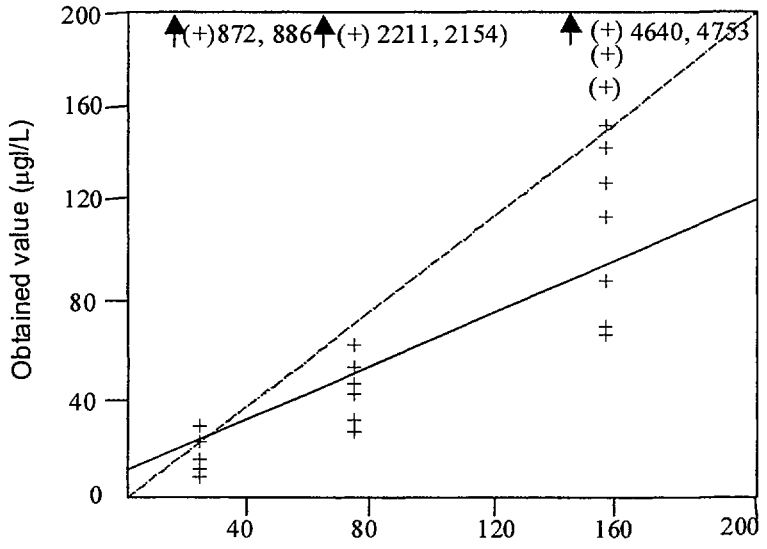


Figure 20. Plot of z-scores of Cr in urine calculated for all laboratories at target value 20.95 µg/L. |Z|-scores > 5 are indicated by an arrow.

Figure 21. Arsenic and cadmium in urine. Results of measurements from six (6) laboratories for arsenic and three laboratories for cadmium.



Regression As

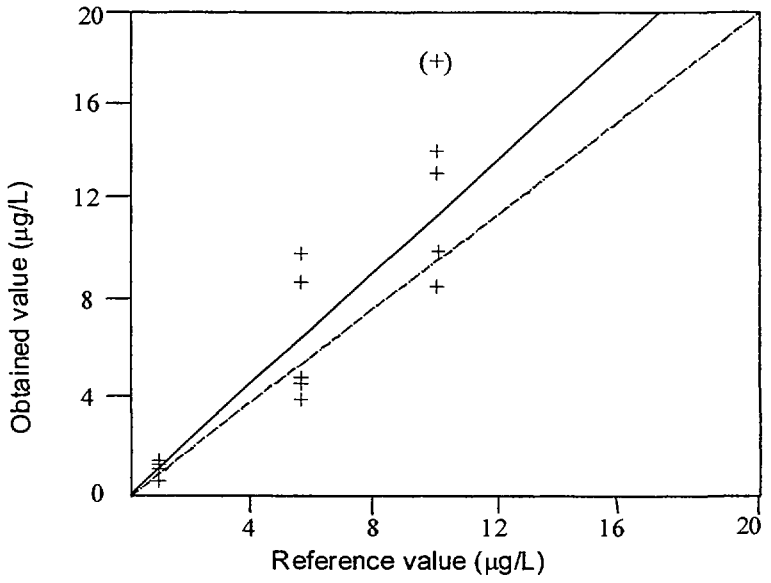
Measured +

Regr.-line ___

Y = X ----

Slope: 0.5511

Intercept: 10.2457



Regression Cd

Measured +

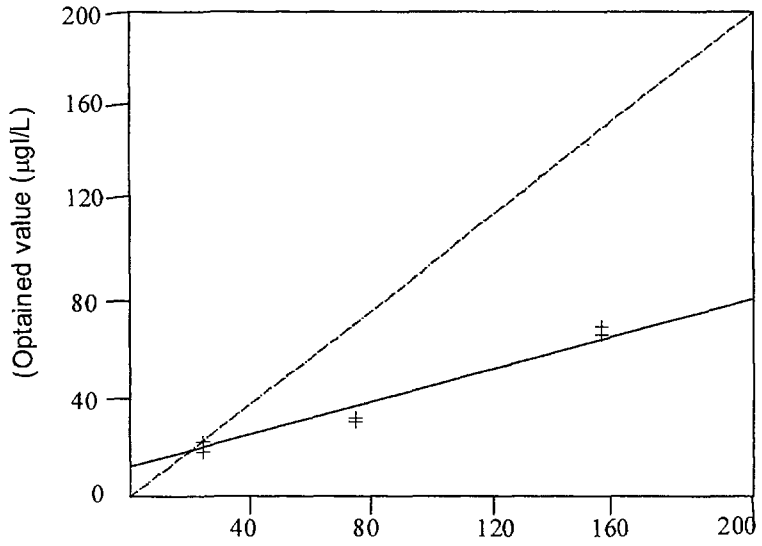
Regr.-line ___

Y = X ----

Slope: 1.1855

Intercept: -0.0524

Figure 22. Arsenic and cadmium in urine. Results of measurements from laboratory 53.



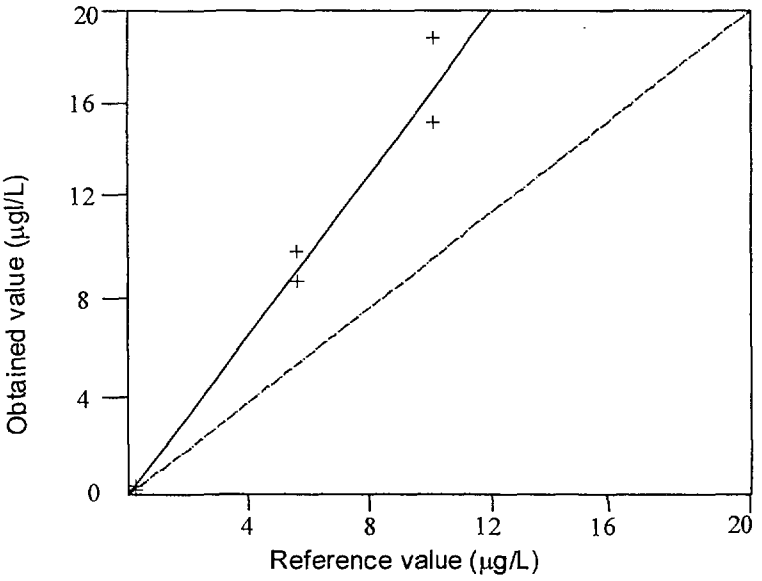
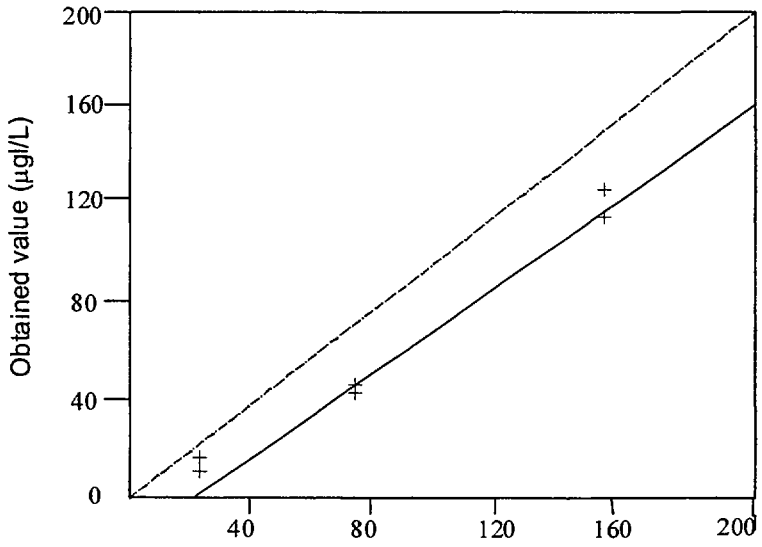


Figure 23. Arsenic and cadmium in urine. Results of measurements from laboratory 58.



Regression As

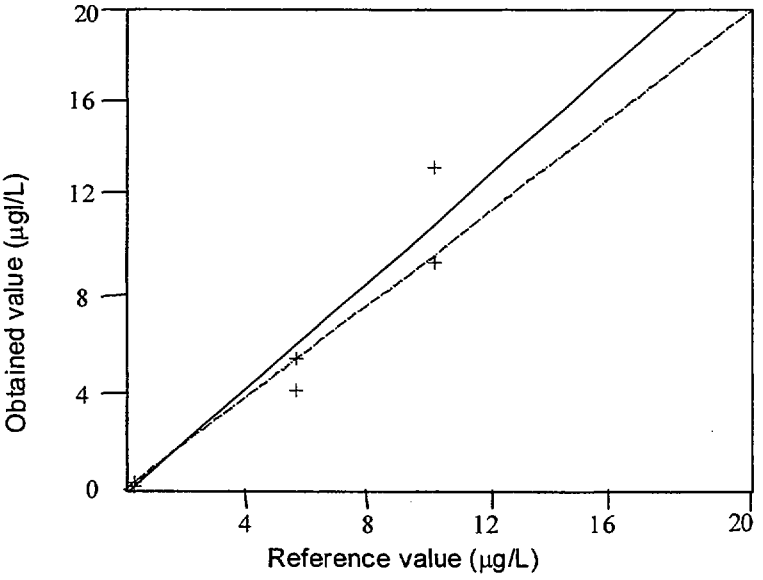
Measured +

Regr.-line ___

Y = X ----

Slope: 0.8738

Intercept: -21.6938



Regression Cd

Measured +

Regr.-line ___

Y = X ----

Slope: 1.1102

Intercept: -0.1693

TABLE II. TARGET VALUE OF CHROMIUM IN WELDING FUME DUST LOADED ON FILTERS, STANDARD UNCERTAINTY, OF TARGET VALUE, OBTAINDED VALUES, DEVIATION FROM TARGET VALUE, RELATIVE STANDARD DEVIATION OF OBTAINED RESULTS, Z-SCORE AND E_n NUMBER.

Component: Chromium in welding fume dust							
Target value: 34.50 ± 1.50 mg/kg dust							
	Results			Deviation	RSD	Z-score	E_n
Lab. #	ID 1	ID 2	Average	%	%		
53	52.1	50.3	51.2	48	2.5	11	6
54	50.8	-	50.8	47	-	11	11
55	30.1	31.6	30.9	-11	3.4	-2	-2
56	53.9	63.6	58.8	70	12	16	4
57	62.5	59.2	60.9	76	3.8	18	12
58	40.3	37.5	38.9	13	5.1	3	2
59	43.2	-	43.2	25	-	6	6
60	46.0	-	46.0	33	-	8	8
All	**47.6**	**48.4**	**47.8**	**38**	**5.3**	**9**	**6**

TABLE III. TARGET VALUE OF MANGANESE IN WELDING FUME DUST LOADED ON FILTERS, STANDARD UNCERTAINTY, OF TARGET VALUE, OBTAINDED VALUES, DEVIATION FROM TARGET VALUE (D), Z-SCORE (Z-SC.) AND MEAN OF ACCEPTED RESULTS (ALL).

Component: Manganese in welding fume dust												
	Target value: 23.0 ± 2.0 µg/filter				Target value: 41.0 ± 3.0 µg/filter				Target value: 89.0 ± 4.5 µg/filter			
	Results				Results				Results			
Lab	ID 1	ID 2	D %	Z-sc.	ID 3	ID 4	D %	Z-sc.	ID 5	ID 6	D%	Z-sc.
53	25	24	7	1	43	42	4	1	85	86	-4	-1
54	22	-	-4	-1	38	-	-7	-1	78	-	-12	-2
55	14	16	-34	-4	21	25	-44	-6	38	44	-54	-11
56	22	21	-7	-1	43	41	5	1	87	82	-5	-1
57	31	-	35	4	55	-	35	5	114	-	28	6
58	19	21	-13	-2	32	34	-20	-3	104	112	21	4
59	21	-	-9	-1	37	-	-10	1	78	-	13	-3
60	23	23	1	0	42	42	2	0	85	85	4	-1
59*	28	-	22	1	48	-	17	2	94	-	6	1
All	**23**	**21**	**0**	**0**	**40**	**37**	**-2**	**0**	**85**	**82**	**0**	**-1**

* Using XRF

TABLE IV. TARGET VALUE OF IRON IN WELDING FUME DUST LOADED ON FILTERS, STANDARD UNCERTAINTY, OF TARGET VALUE, OBTAINDED VALUES, DEVIATION FROM TARGET VALUE (D), Z-SCORE (Z-SC.) AND MEAN OF ACCEPTED RESULTS (ALL).

Component: Iron in welding fume dust												
	Target value: 45.0 ± 5.0 µg/filter				Target value: 82.0±7.0 µg/filter				Target value: 239.0 ±24.5 µg/filter			
	Results				Results				Results			
Lab	ID 1	ID 2	D %	Z-sc.	ID 3	ID 4	D %	Z-sc.	ID 5	ID 6	D%	Z-sc.
53	32	34	-27	2	58	61	-27	-3	164	169	-30	-3
54	42	-	-7	1	86	-	5	1	240	-	0	0
55	62	64	40	4	95	114	28	3	216	240	-5	0
56	43	40	-8	-1	95	85	10	1	225	225	-6	-1
57	66	-	47	4	119	-	45	5	337	-	41	4
58	77	87	82	7	140	153	79	9	412	454	81	8
59	39	57	7	0	69	97	2	0	207	264	-2	0
60	46	-	2	0	84	-	2	0	235	-	-2	0
59*	57	-	27	2	97	-	18	2	264	-	10	1
All	**52**	**56**	**18**	**2**	**94**	**102**	**18**	**2**	**255**	**270**	**10**	**1**

*Using XRF

TABLE V. TARGET VALUE OF TITANIUM IN WELDING FUME DUST LOADED ON FILTERS, STANDARD UNCERTAINTY, OF TARGET VALUE, OBTAINDED VALUES, DEVIATION FROM TARGET VALUE (D), Z-SCORE (Z-SC.) AND MEAN OF ACCEPTED RESULTS (ALL).

Component: Titanium in welding fume dust												
	Target value: 3.5 ± 0.5 µg/filter				Target value: 6.0 ± 0.6 µg/filter				Target value: 14.0 ± 1.4 µg/filter			
	Results				Results				Results			
Lab	ID 1	ID 2	D %	Z-sc.	ID 3	ID 4	D %	Z-sc.	ID 5	ID 6	D%	Z-sc.
53	4	4	14	1	6.0	6	0	0	16.0	16	14	2
54	-	-	-	-	-	-	-	-	21.0	-	50	5
55	3.1	3.4	-6	1	5.7	5.7	-6	-1	11.9	13.5	-10	-1
56	4.6	4.0	22	2	13.6	10.7	103	10	18.2	18.5	31	3
57	8.7	-	148	10	10.5	-	75	8	37.6	-	169	17
58	14.0	15.0	314	22	23.0	25.0	300	30	79.0	83.0	479	48
59	2.5	-	-29	-2	6.9	-	15	2	14.8	-	6	1
60	4.1	3.8	12	1	6.1	6.4	5	1	18.3	16.6	25	2
59*	3.4	-	-3	0	7.0	-	17	2	19.0	-	36	4
All	**4.9**	**6.0**	**59**	**4**	**9.9**	**10.8**	**64**	**7**	**26.2**	**29.5**	**89**	**9**

* Using XRF

TABLE VI. TARGET VALUE OF ARSENIC IN URINE, STANDARD UNCERTAINTY, OF TARGET VALUE, OBTAINDED VALUES, DEVIATION FROM TARGET VALUE (D), Z-SCORE (Z-SC.), AND MEAN OF ACCEPTED RESULTS (ALL).

Component: Arsenic in urine												
	Target value: 23.45 ±1.02 µg/L				**Target value: 75.75 ±1.37 µg/L**				**Target value: 157.0 ±9 µg/L**			
	Results				**Results**				**Results**			
Lab	LO 1	LO 2	D %	Z-sc.	ME 3	ME 4	D %	Z-sc.	HI 5	HI 6	D%	Z-sc.
53	22.8	22.3	-4	-1	33.6	32.4	-56	-31	66	69	-57	-10
54	30.0	-	28	6	41.0	-	-46	-25	87	-	-45	-8
55	-	-	-	-	-	-	-	-	-	-	-	-
56	17.0	-	-28	-6	62.0	-	-18	-10	153	145	-5	-1
57	<105	<102	-	-	<102	<95	-	-	183	166	11	2
58	13.0	17.0	-36	-8	42.0	47.0	-41	-23	115	126	-23	-4
59	30.5	31.0	31	7	77.6	75.6	1	1	164	168	6	1
All	**22.6**	**23.5**	**-2**	**-1**	**51.2**	**52.7**	**-32**	**-18**	**128**	**134**	**-19**	**-3**

TABLE VII. TARGET VALUE OF CADMIUM IN URINE, STANDARD UNCERTAINTY, OF TARGET VALUE, OBTAINDED VALUES, DEVIATION FROM TARGET VALUE (D), Z-SCORE (Z-SC.), AND MEAN OF ACCEPTED RESULTS (ALL).

Component: Cadmium in urine												
	Target value: 0.20 ± 0.02 µg/L				**Target value: 5.20 ± 0.10 µg/L**				**Target value:10.10 ± 0.20 µg/L**			
	Results				**Results**				**Results**			
Lab	LO 1	LO 2	D %	Z-sc.	ME 3	ME 4	D %	Z-sc.	HI 5	HI 6	D%	Z-sc.
53	0.5	0.5	150	15	8.6	10.0	79	41	14.4	17.9	60	30
54	-	-	-	-	-	-	-	-	-	-	-	-
55	0.5	0.55	163	10	4.8	4.0	-16	-8	9.3	9.3	-8	-4
56	-	-	-	-	-	-	-	-	-	-	-	-
57	-	-	-	-	-	-	-	-	-	-	-	-
58	0.5	0.5	150	15	4.4	5.0	-10	-5	10.0	13.0	14	7
59	<50	<40	-	-	<50	<60		-	<80	<90	-	-
All	**0.5**	**0.52**	**154**	**13**	**5.9**	**6.3**	**18**	**9**	**11.2**	**13.4**	**22**	**11**

TABLE VIII. TARGET VALUE OF COBALT IN URINE, STANDARD UNCERTAINTY, OF TARGET VALUE, OBTAINDED VALUES, DEVIATION FROM TARGET VALUE (D), Z-SCORE (Z-SC.), AND MEAN OF ACCEPTED RESULTS (ALL).

Component: Cobalt in urine												
	Target value: 0.31±0.11 µg/L				Target value: 10.45 ±0.51 µg/L				Target value: 61.70±2.20 µg/L			
	Results				Results				Results			
Lab	LO 1	LO 2	D %	Z-sc.	ME 3	ME 4	D %	Z-sc.	HI 5	HI 6	D%	Z-sc.
53	0.5	0.5	61	2	8.2	8.4	-20	-4	40.8	36.0	-38	-11
54	-	-	-	-	50.0	-	379	78	200.0	-	224	63
55	-	-	-	-	-	-	-	-	-	-	-	-
56	27.0		8610	243	35.0		236	48	63.0	73.0	10	3
57	<88	<75	-	-	<71	<71	-	-	<116	<95	-	-
58	-	-	-	-	-	-	-	-	-	-	-	-
59	0.27	0.23	-19	-1	11.0	10.7	4	1	66.0	68.1	9	2
All	**9.3**	**0.36**	**2884**	**81**	**26.0**	**10**	**148**	**30**	**92.5**	**59.0**	**51**	**14**

TABLE IX. TARGET VALUE OF CHROMIUM IN URINE, STANDARD UNCERTAINTY, OF TARGET VALUE, OBTAINDED VALUES, DEVIATION FROM TARGET VALUE (D), Z-SCORE (Z-SC.), AND MEAN OF ACCEPTED RESULTS (ALL).

Component: Chromium in urine												
	Target value: 1.47 ± 0.23 µg/L				Target value: 6.44 ± 0.41 µg/L				Target value:20.95 ± 0.84 µg/L			
	Results				Results				Results			
Lab	LO 1	LO 2	D %	Z-sc.	ME 3	ME 4	D %	Z-sc.	HI 5	HI 6	D%	Z-sc.
53	11.1	12.3	696	44	22.3	27.8	289	45	46.3	44.7	117	29
54	-	-	-	-	-	-	-	-	-	-	-	-
55	-	-	-	-	-	-	-	-	-	-	-	-
56	560	-	37995	2428	370	-	5645	887	247	303	1213	302
57	<95	<82	-	-	<102	<95	-	-	<126	<95	-	-
58	-	-	-	-	-	-	-	-	-	-	-	-
59	<1.5	<2	-	-	8.9	5.1	52	8	20.7	20.9	-1	0
All	**285**	**12.3**	**19347**	**1236**	**134**	**16.4**	**1995**	**313**	**105**	**123**	**443**	**110**