

Round-robin tests for in-house measuring laboratories

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Results and Evaluation

Round-robin test

Metals- dust 2015

Summary of laboratory means

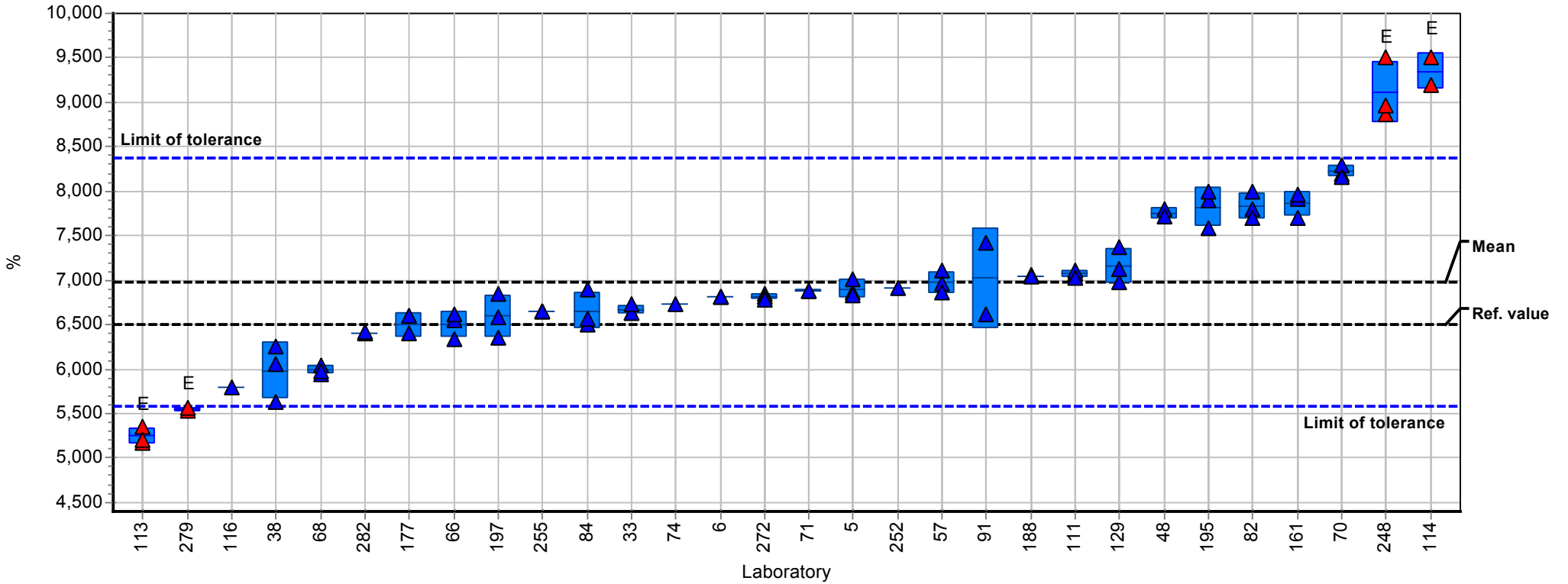
Sample 1

| Unit | chromium Z score | | copper Z score | | mangan Z score | | nickel Z score | | zinc Z score | | iron Z score | |
|------|------------------|---------|----------------|---------|----------------|---------|----------------|--------|--------------|---------|--------------|---------|
| | % | | % | | % | | % | | % | | % | |
| 5 | 6,903 | -0,11 | 0,4663 | 0,28 | 22,38 | 0,29 | 3,288 | -0,17 | 0,2227 | -0,30 | 26,41 | -0,10 |
| 6 | 6,811 | -0,24 | 0,4602 | 0,14 | 21,62 | -0,06 | 3,381 | 0,11 | 0,2282 | -0,06 | 26,35 | -0,13 |
| 33 | 6,670 | -0,45 | 0,4413 | -0,27 | 21,67 | -0,03 | 3,170 | -0,52 | 0,2207 | -0,39 | 25,83 | -0,32 |
| 38 | 5,983 | -1,43 | 0,4200 | -0,74 | 20,01 | -0,80 | 2,997 | -1,04 | 0,2033 | -1,14 | 22,82 | -1,45 |
| 48 | 7,755 | 1,11 | 0,4300 | -0,52 | 23,39 | 0,76 | 3,740 | 1,18 | 0,3050 | 3,29 BE | 34,68 | 2,99 E |
| 57 | 6,975 | -0,01 | 0,4657 | 0,26 | 21,26 | -0,22 | 2,967 | -1,13 | 0,2233 | -0,27 | 25,22 | -0,55 |
| 66 | 6,500 | -0,69 | 0,4303 | -0,51 | 19,71 | -0,94 | 3,190 | -0,46 | 0,2367 | 0,31 | 22,83 | -1,45 |
| 68 | 5,987 | -1,42 | 0,4263 | -0,60 | 21,73 | 0,00 | 2,953 | -1,17 | 0,2457 | 0,70 | 24,80 | -0,71 |
| 70 | 8,222 | 1,78 | 0,4423 | -0,25 | 21,95 | 0,09 | 3,617 | 0,82 | 0,2321 | 0,11 | 29,05 | 0,89 |
| 71 | 6,880 | -0,14 | 0,4485 | -0,11 | 21,65 | -0,04 | 3,293 | -0,15 | 0,2255 | -0,18 | 26,30 | -0,15 |
| 74 | 6,730 | -0,36 | 0,4400 | -0,30 | 20,22 | -0,70 | 3,100 | -0,73 | 0,2100 | -0,85 | 25,46 | -0,46 |
| 82 | 7,833 | 1,22 | 0,5267 | 1,61 | 23,70 | 0,90 | 4,100 | 2,26 E | 0,3233 | 4,09 CE | 30,57 | 1,45 |
| 84 | 6,657 | -0,46 | 0,4587 | 0,11 | 20,61 | -0,52 | 3,343 | 0,00 | 0,2293 | -0,01 | 24,61 | -0,78 |
| 91 | 7,020 | 0,06 | 0,4850 | 0,69 | 21,92 | 0,08 | 3,300 | -0,13 | 0,2250 | -0,20 | 25,31 | -0,51 |
| 111 | 7,070 | 0,13 | 0,4833 | 0,65 | 22,77 | 0,47 | 3,427 | 0,25 | 0,2433 | 0,60 | 27,73 | 0,39 |
| 113 | 5,247 | -2,48 E | 0,3827 | -1,56 | 19,64 | -0,97 | 2,823 | -1,56 | 0,1907 | -1,69 | 19,89 | -2,55 E |
| 114 | 9,350 | 3,39 E | 0,5300 | 1,68 | 25,00 | 1,50 | 4,050 | 2,11 E | 0,2700 | 1,76 | 32,50 | 2,18 E |
| 116 | 5,790 | -1,71 | 0,4300 | -0,52 | 24,81 | 1,41 | 2,870 | -1,42 | 0,1900 | -1,72 | 26,58 | -0,04 |
| 129 | 7,156 | 0,25 | 0,4367 | -0,37 | 20,33 | -0,65 | 3,136 | -0,62 | 0,2293 | -0,01 | 24,86 | -0,68 |
| 161 | 7,860 | 1,26 | 0,5700 | 2,56 BE | 30,18 | 3,88 BE | 3,973 | 1,88 | 0,2767 | 2,05 E | 32,39 | 2,14 E |
| 177 | 6,500 | -0,69 | 0,4667 | 0,29 | 22,77 | 0,47 | 3,450 | 0,31 | 0,2333 | 0,17 | 27,07 | 0,14 |
| 188 | 7,050 | 0,10 | 0,4503 | -0,07 | 21,35 | -0,18 | 3,367 | 0,07 | 0,2267 | -0,12 | 26,49 | -0,07 |
| 195 | 7,823 | 1,21 | 0,4433 | -0,23 | 19,80 | -0,89 | 3,437 | 0,27 | 0,2433 | 0,60 | 25,68 | -0,38 |
| 197 | 6,597 | -0,55 | 0,4277 | -0,57 | 21,83 | 0,04 | 3,143 | -0,60 | 0,2153 | -0,62 | 25,87 | -0,31 |
| 248 | 9,117 | 3,06 E | 0,5033 | 1,10 | 22,78 | 0,48 | 4,063 | 2,15 E | 0,2367 | 0,31 | 29,94 | 1,22 |
| 252 | 6,920 | -0,09 | 0,4500 | -0,08 | 23,69 | 0,90 | 3,320 | -0,07 | 0,2300 | 0,02 | 27,49 | 0,30 |
| 255 | 6,650 | -0,47 | 0,4640 | 0,23 | 21,50 | -0,11 | 3,200 | -0,43 | 0,2290 | -0,02 | 27,50 | 0,30 |
| 272 | 6,816 | -0,24 | 0,4597 | 0,13 | 23,53 | 0,82 | 3,297 | -0,14 | 0,2293 | -0,01 | 27,85 | 0,43 |

| | chromium Z score | copper Z score | mangan Z score | nickel Z score | zinc Z score | iron Z score |
|--|------------------|----------------|----------------|----------------|--------------|--------------|
| 279 | 5,545 -2,06 E | 0,4470 -0,15 | 20,70 -0,48 | 2,960 -1,15 | 0,2350 0,24 | |
| 282 | 6,403 -0,83 | 0,4366 -0,38 | 21,50 -0,11 | 3,130 -0,64 | 0,2210 -0,37 | 25,54 -0,43 |
| | -- | -- | -- | -- | -- | -- |
| Method | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 | ISO 5725-2 |
| Assessment | Z <=2,00 | Z <=2,00 | Z <=2,00 | Z <=2,00 | Z <=2,00 | Z <=2,00 |
| No. of laboratories that submitted results | 30 | 30 | 30 | 30 | 30 | 29 |
| Mean | 6,981 | 0,4536 | 21,74 | 3,345 | 0,2295 | 26,69 |
| Reproducibility s.d. | 0,917 | 0,0325 | 1,40 | 0,363 | 0,0193 | 3,08 |
| Rel. reproducibility s.d. | 13,13 % | 7,17 % | 6,42 % | 10,85 % | 8,41 % | 11,54 % |
| Reference value | 6,494 | 0,4317 | 22,08 | 3,089 | 0,2187 | 25,25 |
| Target s.d. | 0,698 | 0,0454 | 2,17 | 0,334 | 0,0230 | 2,67 |
| Rel. target s.d.: | 10,00 % | 10,00 % | 10,00 % | 10,00 % | 10,00 % | 10,00 % |
| Lower limit of tolerance | 5,585 | 0,3629 | 17,39 | 2,676 | 0,1836 | 21,35 |
| Upper limit of tolerance | 8,377 | 0,5444 | 26,09 | 4,014 | 0,2754 | 32,03 |
| Type B outliers | | 1 | 1 | | 1 | |
| Number of laboratories with replicates outside of tolerance limits | 4 | 2 | 1 | 4 | 4 | 4 |
| No. of laboratories after elimination of outliers type A-D and F (without laboratories that only gave states but no measured values) | 30 | 29 | 29 | 30 | 28 | 29 |
| Explanation of outlier types | | | | | | |
| A: Single outlier | Grubbs | | | | | |
| B: Differing laboratory mean | Grubbs | | | | | |
| C: Excessive laboratory s.d. | Cochran | | | | | |
| D: Excluded manually | | | | | | |
| E: mean outside tolerance limits | | | | | | |
| F: Z-Score >3,5 | | | | | | |

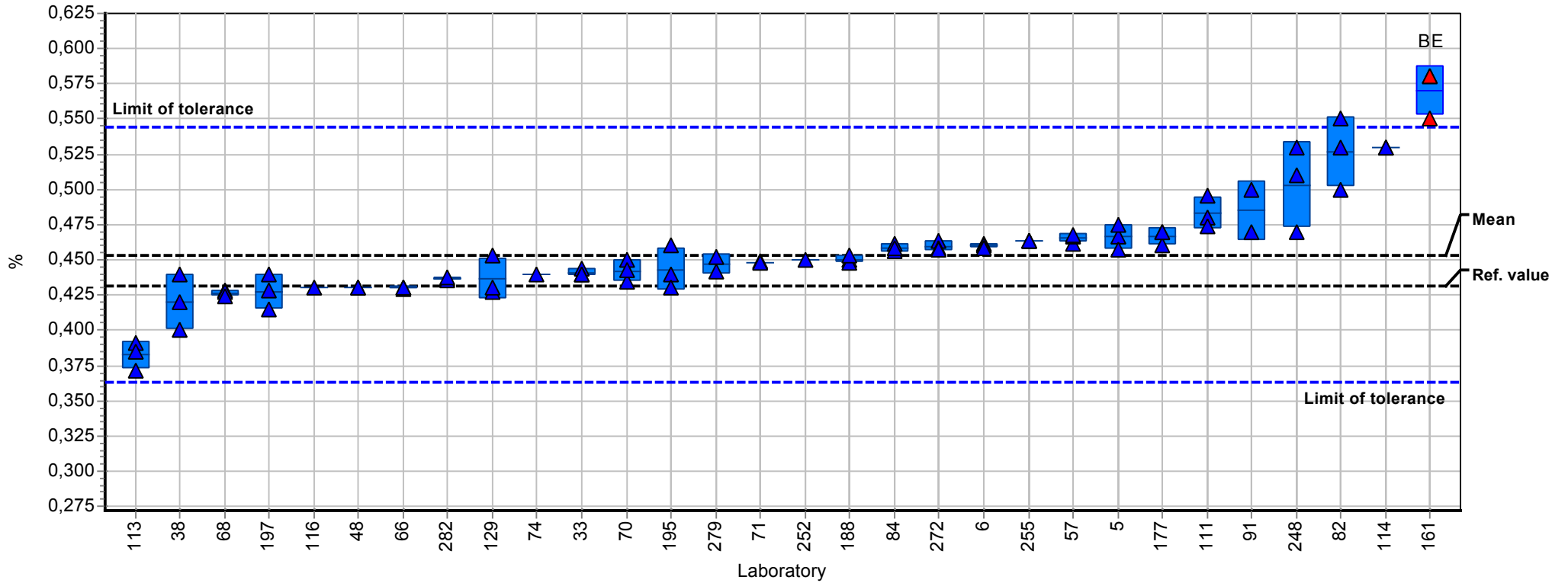
Summary results

| | | | |
|------------------------------|------------------|---------------------------------------|---------------------------------------|
| Measurand: | chromium | Mean: | 6,9811 % |
| Sample: | 1 | Reproducibility s.d.: | 0,9165 % |
| Method: | ISO 5725-2 | Relative reproducibility s.d.: | 13,13% |
| No. of laboratories: | 30 | Reference value: | 6,4940 % |
| Relative target s.d.: | 10,00% (Limited) | Range of tolerance: | 5,5849 - 8,3774 % (Z-Score <= 2,00) |



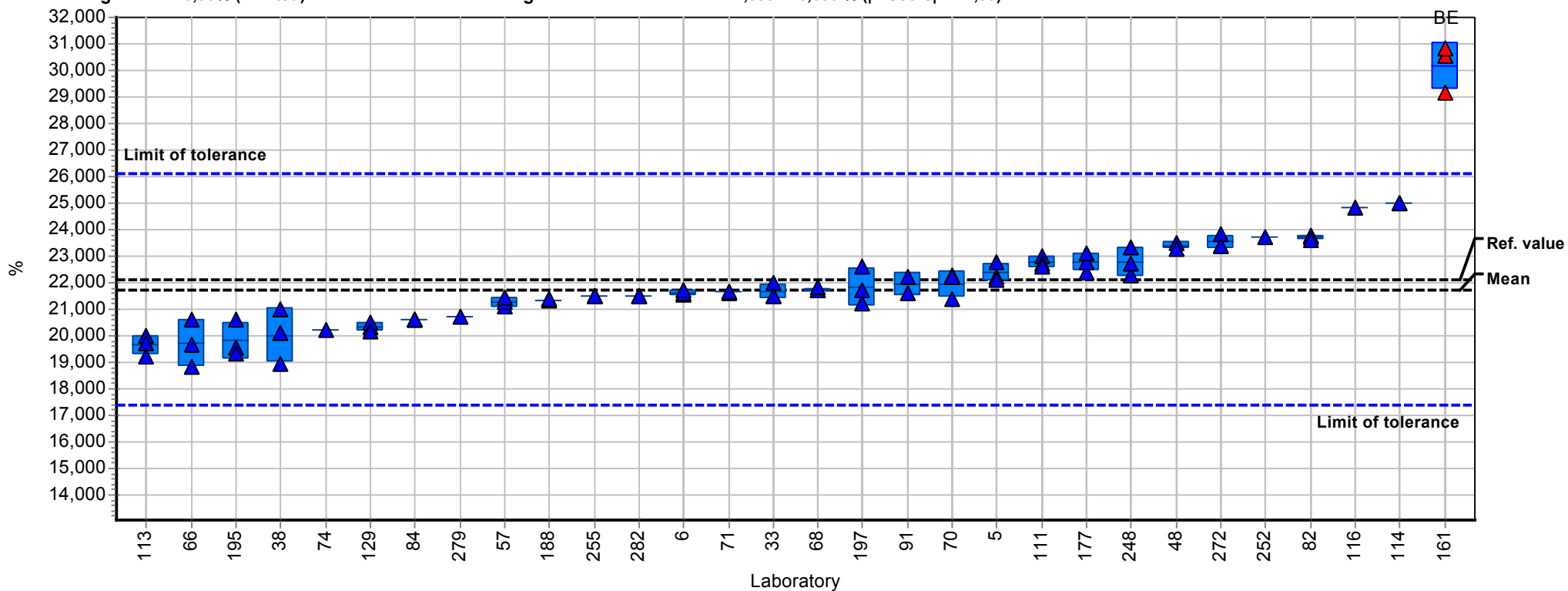
Summary results

| | | | |
|------------------------------|------------------|---------------------------------------|---------------------------------------|
| Measurand: | copper | Mean: | 0,4536 % |
| Sample: | 1 | Reproducibility s.d.: | 0,0325 % |
| Method: | ISO 5725-2 | Relative reproducibility s.d.: | 7,17% |
| No. of laboratories: | 29 | Reference value: | 0,4317 % |
| Relative target s.d.: | 10,00% (Limited) | Range of tolerance: | 0,3629 - 0,5444 % (Z-Score <= 2,00) |



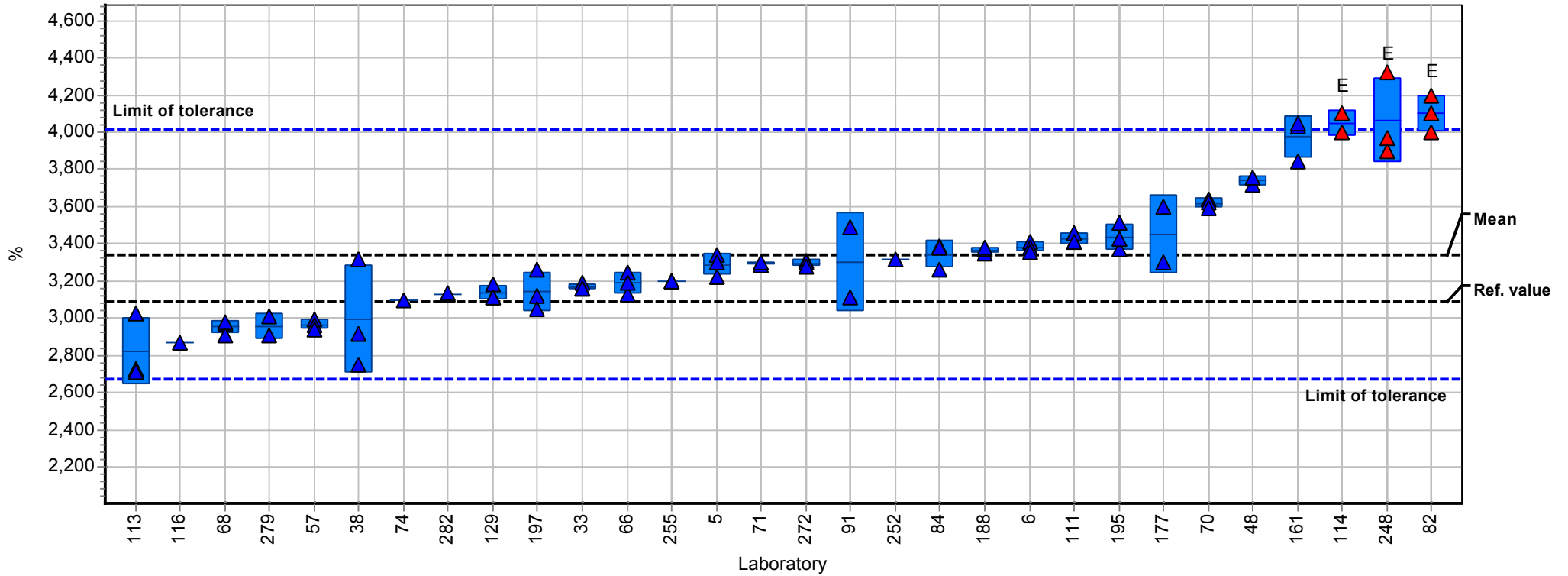
Summary results

| | | | |
|------------------------------|------------------|---------------------------------------|---------------------------------------|
| Measurand: | mangan | Mean: | 21,741 % |
| Sample: | 1 | Reproducibility s.d.: | 1,395 % |
| Method: | ISO 5725-2 | Relative reproducibility s.d.: | 6,42% |
| No. of laboratories: | 29 | Reference value: | 22,080 % |
| Relative target s.d.: | 10,00% (Limited) | Range of tolerance: | 17,393 - 26,090 % (Z-Score <= 2,00) |



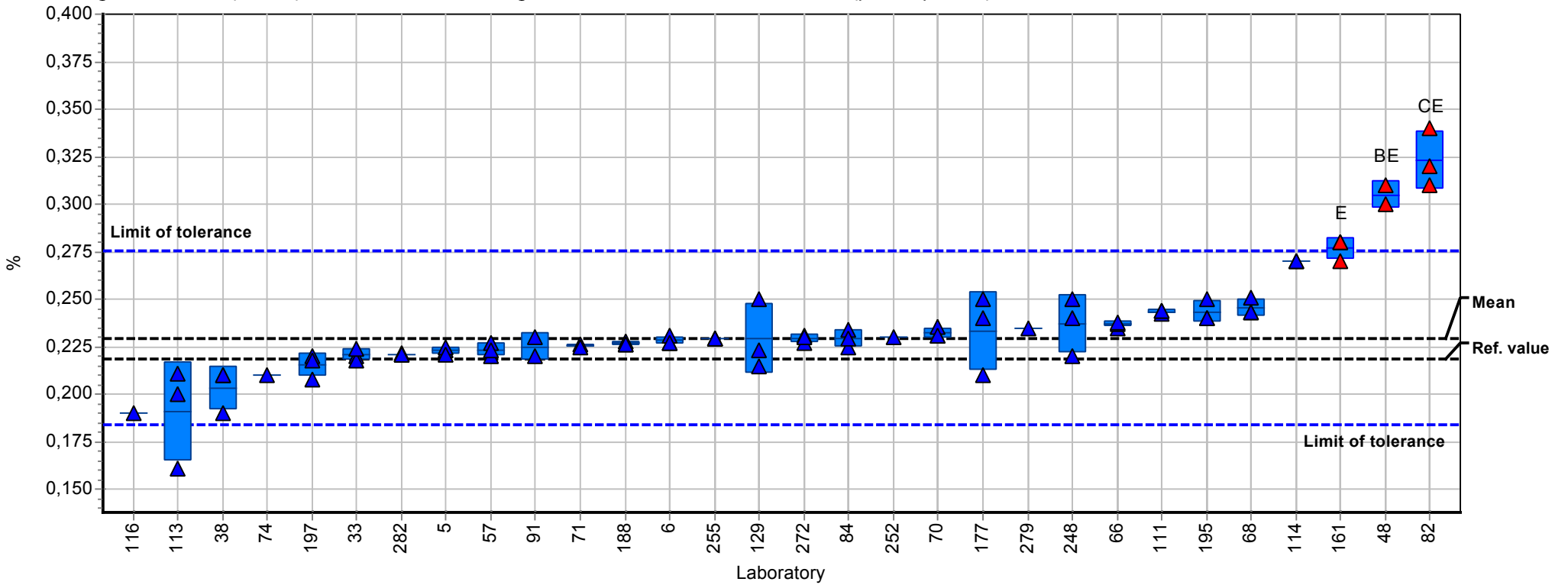
Summary results

| | | | |
|-----------------------|------------------|--------------------------------|-------------------------------------|
| Measurand: | nickel | Mean: | 3,345 % |
| Sample: | 1 | Reproducibility s.d.: | 0,363 % |
| Method: | ISO 5725-2 | Relative reproducibility s.d.: | 10,85% |
| No. of laboratories: | 30 | Reference value: | 3,089 % |
| Relative target s.d.: | 10,00% (Limited) | Range of tolerance: | 2,676 - 4,014 % (Z-Score <= 2,00) |



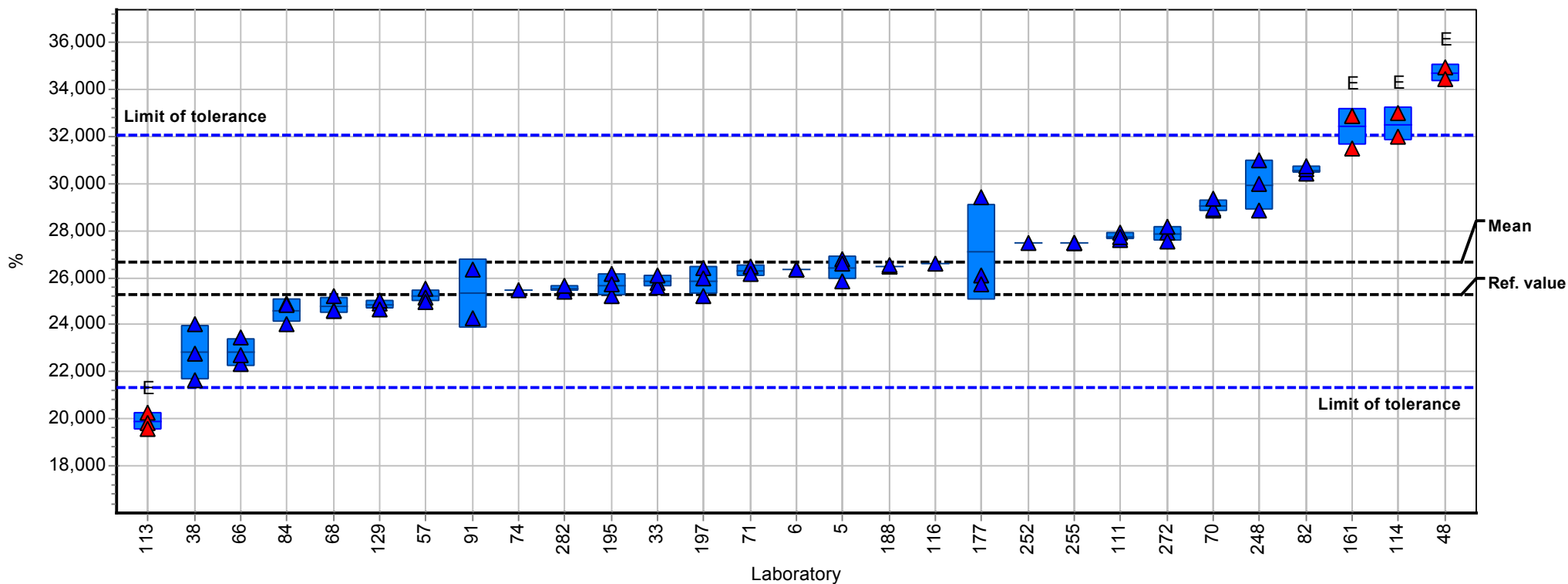
Summary results

| | | | |
|------------------------------|------------------|---------------------------------------|---------------------------------------|
| Measurand: | zinc | Mean: | 0,2295 % |
| Sample: | 1 | Reproducibility s.d.: | 0,0193 % |
| Method: | ISO 5725-2 | Relative reproducibility s.d.: | 8,41% |
| No. of laboratories: | 28 | Reference value: | 0,2187 % |
| Relative target s.d.: | 10,00% (Limited) | Range of tolerance: | 0,1836 - 0,2754 % (Z-Score <= 2,00) |



Summary results

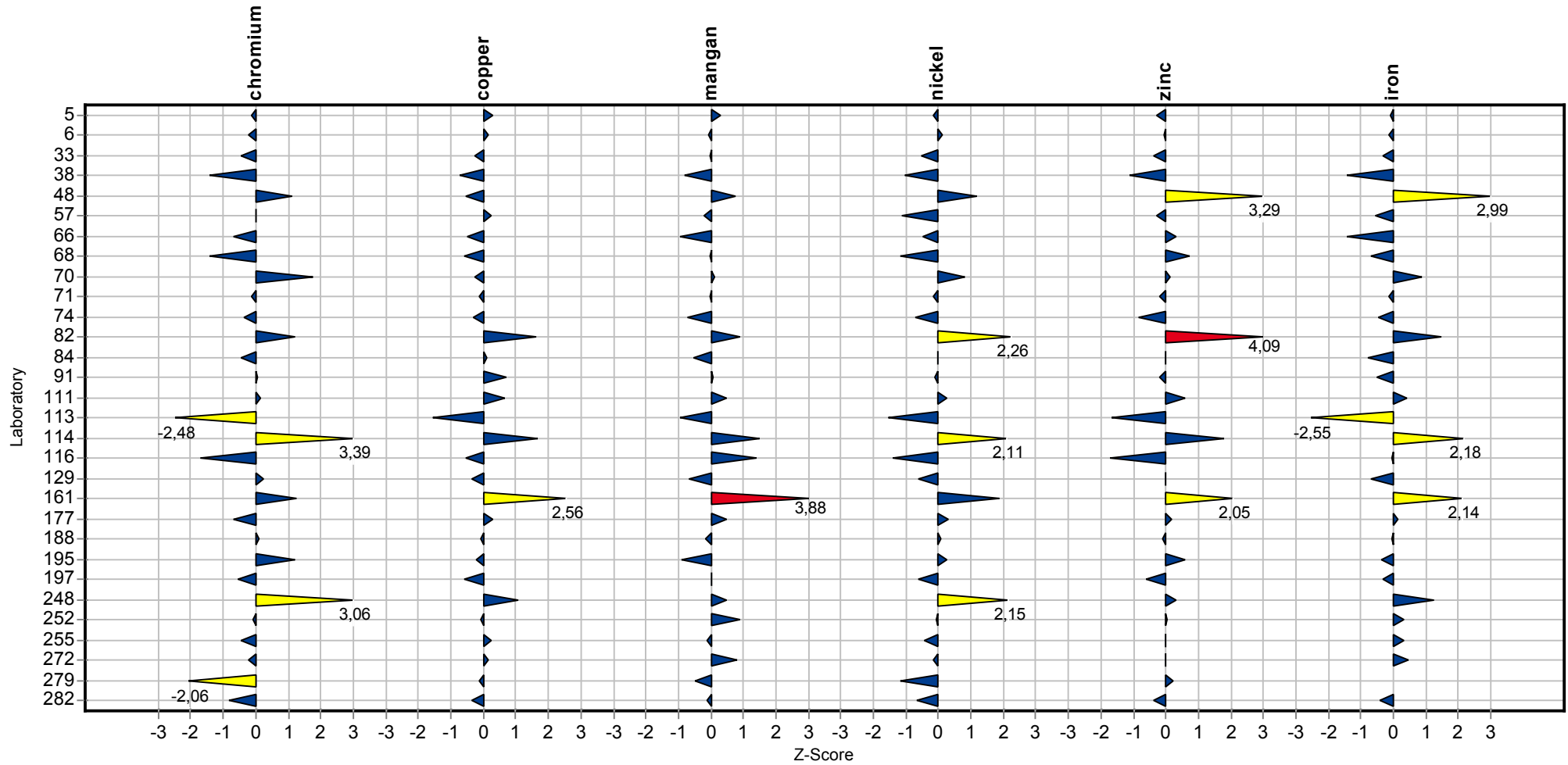
| | | | |
|------------------------------|------------------|---------------------------------------|-------------------------------------|
| Measurand: | iron | Mean: | 26,69 % |
| Sample: | 1 | Reproducibility s.d.: | 3,08 % |
| Method: | ISO 5725-2 | Relative reproducibility s.d.: | 11,54% |
| No. of laboratories: | 29 | Reference value: | 25,25 % |
| Relative target s.d.: | 10,00% (Limited) | Range of tolerance: | 21,35 - 32,03 % (Z-Score <= 2,00) |



Sample chart of Z-Scores

Sample 1

Measurand



Questions and Answers

| Participant | pulping method | acid concentration |
|-------------|--|---|
| 5 | Blatt 6015 | |
| 6 | IFA-Arbeitsmappe Blatt 6015 | HNO3 65% HCl 25% |
| 33 | IFA-Arbeitsmappe, Blatt 6015 | Salpetersäure (65%) ; Salzsäure (25%) |
| 38 | IFA-Arbeitsmappe, Blatt 6015 | HNO3 69%, HCl 30% |
| 48 | IFA-working folder, sheet 6015 | %65 HNO3 , %30 HCl |
| 57 | Standardaufschluss nach IFA | HNO3 65 %, HCl 25 % |
| 66 | ja | Salpetersäure 65 %, Salzsäure 37 % |
| 68 | IFA-Arbeitsmappe | HNO3 65% und HCl 37% |
| 70 | Königswasseraufschluss | 65%ige Salpetersäure, 30%ige Salzsäure |
| 71 | IFA-Arbeitsmappe, blatt 6015 | HNO3 65%ig , HCl 30%ig |
| 74 | IFA-Arbeitsmappe, Blatt 6015 | Salpetersäure 65%, Salzsäure 25% |
| 82 | IFA Blatt 6015 | HNO3 65% HCl 30% |
| 84 | ja | HCl 37%, HNO3 65% |
| 91 | IFA Arbeitsmappe, Blatt6015 | IFA Arbeitsmappe, Blatt6015 |
| 111 | IFA 6015 | 65% HNO3, 25% HCl |
| 113 | IFA Blatt 6015 | HCL 32% und HNO3 65% |
| 114 | According to IFA-working folder (sheet 6015) but with light modification, microwave digestion method | HNO3 69% and HCl 30% |
| 116 | | HNO3 65%, HCl 30% |
| 129 | IFA- Arbeitsmappe, Blatt 6015 | HCL: 30% ; HNO3: 65% |
| 161 | IFA-Arbeitsblatt | 65% Salpetersäure und 25% Salzsäure |
| 177 | IFA-Arbeitsmappe, Blatt 6015 | HNO3 (65%) HCl (25%) |
| 188 | IFA, Arbeitsmappe 6015 | HCl suprapur 30%ig, HNO3 suprapur 65%ig |
| 195 | internal method based on NIOSH n° 7300 "Elements by ICP" Rev. 2 | 2,5 mL Nitric acid (69%):2,5 mL hydrogen peroxide |
| 197 | nach Beilage zum RV | 65%HNO3/25% HCl |
| 248 | ifa 6015 | HNO3 65 %, HCl 30% |
| 252 | IFA 6015 | IFA 6015 |
| 255 | IFA 6015 | HNO3 (65 %) / HCl (25 %) |
| 272 | IFA-Arbeitsmappe, Blatt 6015 | HNO3 65% v/v, HCl 25% v/v |
| 279 | Aufschlußmethode: IFA-Arbeitsmappe Blatt 6015 | HNO3: 65 %ig HCl: 25 %ig |
| 282 | IFA-Arbeitsmappe, Blatt 6015 | HNO3 65%; HCl 25% |

Round-robin test Metals 2015

| Participant | mixing ratio | dust weight | time of pulping | pressure pulping | reagent volume |
|-------------|---|-----------------------------|-------------------|------------------|---|
| 6 | 2:1 | 10 | 2 | Nein | 100 |
| 33 | 2 Volumenteile Salpetersäure; 1 Volumenteil Salzsäure | 30 | 2 | Nein | 100 |
| 38 | 6 ml HNO ₃ , 3 ml HCl | 20 | 2 | nein | 50 |
| 48 | 2:1 | 10 mg | 2 | no | 10 mL |
| 57 | 2 : 1 | 20 | 2 | Nein | 50 |
| 66 | 2:1 | 20 - 25 mg | 2 | nein | 50 |
| 68 | 2:1 | ca. 20 mg | 2 Std. | Nein | 50 ml |
| 70 | 8 ml Salpetersäure : 4 ml Salzsäure | ca. genau 20 mg | 2 h | nein | 20 ml |
| 71 | 13 mL HNO ₃ : 6,5 mL HCl | 50,01 mg | 2 h | nein | 50 mL |
| 74 | 2 Volumenteile HNO ₃ , 1 Volumenteil HCl | ca. 20 | 2 | Nein | 50 |
| 82 | 2:1 | ~20 mg | 2h | Nein | 20 ml |
| 84 | 1:2 | 10-20 mg | 2h | Nein | 50 ml |
| 91 | IFA Arbeitsmappe, Blatt6015 | IFA Arbeitsmappe, Blatt6015 | 2 | nein | 20 |
| 111 | 2:1 | 20 | 2 | nein | 20 |
| 113 | 2 : 1 | ca. 15 - 26mg | 2 | Nein | 50 |
| 114 | 2/1 | 22.4 | 45 mins | yes | 6 |
| 116 | 2/1 | 20 | 2 | Nein | 20 |
| 129 | HCL:HNO ₃ : 1:2 | 20mg | 2 | Nein | 25 |
| 161 | 2:1 | ca. 50 mg | 120 min | Nein | 20 ml |
| 177 | 2:1 (HNO ₃ : HCl) | Je ca. 20 mg | 2h unter Rückfluß | Nein | 100 mL |
| 188 | gem. Vorgabe | 20mg gem. Vorgabe | 2 | nein | 100 ml |
| 195 | 1:1 | 50 mg aprox. | 0.58 | NO | 4 |
| 197 | 2:1 | 20,6/20,7/21,2 | 2 | | 17 |
| 248 | 2:1 | ca. 20 mg | 1,5 | Ja | Ca. 80 ml |
| 252 | IFA 6015 | 100 | 2 | Nein | Aufgefüllt auf 100 ml, dann 1 auf 10 verdünnt |
| 255 | 2:1 | ca. 20 mg | 2 h | nein | 25 ml bzw. 100 ml |
| 272 | HNO ₃ : HCl = 2:1 | ca. 20 | 2 | Nein | 100 |
| 279 | HNO ₃ : HCl = 2 : 1 | 50 mg und 90 mg | ca. 2- 3 Stunden | nein | 50 ml |
| 282 | 2:1 | 50 mg | 2 h | nein | 50 ml |

| Participant | equipment | method for chromium | method for copper | method for nickel | method for mangan |
|-------------|-----------|---------------------|-------------------|-------------------|-------------------|
| 5 | | ICP-OES | ICP-OES | ICP-OES | ICP-OES |

Round-robin test Metals 2015

| Participant | equipment | method for chromium | method for copper | method for nickel | method for mangan |
|-------------|------------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
| 6 | offen | ICP/OES | ICP/OES | ICP/OES | ICP/OES |
| 33 | offen | DIN EN ISO 17294-2 | DIN EN ISO 17294-2 | DIN EN ISO 17294-2 | DIN EN ISO 17294-2 |
| 38 | geschlossen | ICP-MS | ICP-MS | ICP-MS | ICP-MS |
| 48 | open | ICP/MS | ICP/MS | ICP/MS | ICP/MS |
| 57 | offen | ICP-OES | ICP-OES | ICP-OES | ICP-OES |
| 66 | geschlossen | AAS/Flamme | AAS/Flamme | AAS/Flamme | AAS/Flamme |
| 68 | geschlossen | ICP-OES | ICP-OES | ICP-OES | ICP-OES |
| 70 | offen | ICP/OES | ICP/OES | ICP/OES | ICP/OES |
| 71 | offen | ICP-OES | ICP-OES | ICP-OES | ICP-OES |
| 74 | geschlossene Rückflussdestillation | ICP/OES | ICP/OES | ICP/OES | ICP/OES |
| 82 | offen | | | | |
| 84 | unter Rückfluss | DIN EN ISO 17294-2(E29) ICP-MS | DIN EN ISO 17294-2(E29) ICP-MS | DIN EN ISO 17294-2(E29) ICP-MS | DIN EN ISO 17294-2(E29) ICP-MS |
| 91 | offen | ICP/MS | ICP/MS | ICP/MS | ICP/MS |
| 111 | offen | ICP/MS | ICP/MS | ICP/MS | ICP/MS |
| 113 | offen | ICP-OES | ICP-OES | ICP-OES | ICP-OES |
| 114 | closed | ICPMS | ICPMS | ICPMS | ICPMS |
| 116 | Digiprep | ICP OES | ICP OES | ICP OES | ICP OES |
| 129 | keine Angabe | AAS/Flamme | AAS/Flamme | AAS/Flamme | AAS/Flamme |
| 161 | offen | ICP-OES | ICP-OES | ICP-OES | ICP-OES |
| 177 | offen | ICP-OES | ICP-OES | ICP-OES | ICP-OES |
| 188 | offen | ICP | ICP | ICP | ICP |
| 195 | MW digestion | ICP-OES | ICP-OES | ICP-OES | ICP-OES |
| 197 | | ICp-MS | ICp-MS | ICp-MS | ICp-MS |
| 248 | geschlossen | ICP-OES | ICP-OES | ICP-OES | ICP-OES |
| 252 | offen | ICP-OES | ICP-OES | ICP-OES | ICP-OES |
| 255 | Rückflusskühler | AAS | AAS | AAS | AAS |
| 272 | offener Anschluß unter Rückfluß | ICP-OES | ICP-OES | ICP-OES | ICP-OES |
| 279 | offener Anschluß | AAS-Flamme | AAS-Flamme | AAS-Flamme | AAS-Flamme |
| 282 | geschlossen | ICP-OES | ICP-OES | ICP-OES | ICP-OES |
| Participant | method for zinc | method for iron | | | |
| 5 | ICP-OES | ICP-OES | | | |

Round-robin test Metals 2015

| Participant | method for zinc | method for iron |
|-------------|--------------------------------|--------------------------------|
| 6 | AAS/Flamme | ICP/OES |
| 33 | DIN EN ISO 17294-2 | DIN EN ISO 17294-2 |
| 38 | ICP-MS | ICP-MS |
| 48 | ICP/MS | ICP/MS |
| 57 | ICP-OES | ICP-OES |
| 66 | AAS/Flamme | AAS/Flamme |
| 68 | ICP-OES | ICP-OES |
| 70 | ICP/OES | ICP/OES |
| 71 | ICP-OES | ICP-OES |
| 74 | ICP/OES | ICP/OES |
| 84 | DIN EN ISO 17294-2(E29) ICP-MS | DIN EN ISO 17294-2(E29) ICP-MS |
| 91 | ICP/MS | ICP/MS |
| 111 | ICP/MS | ICP/MS |
| 113 | ICP-OES | ICP-OES |
| 114 | ICPMS | ICPMS |
| 116 | ICP OES | ICP OES |
| 129 | AAS/Flamme | AAS/Flamme |
| 161 | ICP-OES | ICP-OES |
| 177 | ICP-OES | ICP-OES |
| 188 | ICP | ICP |
| 195 | ICP-OES | ICP-OES |
| 197 | ICp-MS | ICP-OES |
| 248 | ICP-OES | ICP-OES |
| 252 | ICP-OES | ICP-OES |
| 255 | AAS | AAS |
| 272 | ICP-OES | ICP-OES |
| 279 | AAS-Flamme | keine Bestimmung durchgeführt |
| 282 | ICP-OES | ICP-OES |