**CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION**

INTERNATIONAL COOPERATIVE PROGRAMME ON ASSESSMENT AND MONITORING OF ACIDIFICATION OF RIVERS AND LAKES

# Intercomparison 9610

pH, $K_{25}$, $HCO_3$, $NO_3$ + $NO_2$, Cl, $SO_4$, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC and COD-Mn

Prepared by the Programme Centre,
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Abstract:

36 laboratories in 21 countries participated in intercomparison 9610. Two sample sets, one for the major ions and one for organic matter and aluminium fractions, were used. Based on the general target accuracy of ± 20 %, 70 % of the results were acceptable. More than 80 % of the result pairs were acceptable for conductivity, nitrate+nitrite, calcium, sodium and dissolved organic carbon. For pH only 55 % of the result pairs were acceptable in relation to the extended target accuracy of ± 0.2 units. For three analytical variables: alkalinity, reactive and non-labile aluminium, it was decided **not** to evaluate the reported results, because of the extreme spread of the results between the participants. Normalization of the methods is necessary to improve the comparability for these variables. High concentration of organic anions in sample A revealed that som laboratories are using methods influenced by interferences, especially for the determination of alkalinity and chloride. Manual methods are generally less sensitive compared to instrumental methods.



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INTERNATIONAL CO-OPERATIVE PROGRAMME FOR ASSESSMENT AND MONITORING OF ACIDIFICATION OF RIVERS AND LAKES

# INTERCOMPARISON 9610

**pH, $\kappa_{25}$, $HCO_3^-$, $NO_3^- + NO_2^-$, $Cl^-$, $SO_4^{--}$**
**$Ca^{++}$, $Mg^{++}$, $Na^+$, $K^+$, Al, Al-R, Al-I, DOC and COD-Mn**

Oslo, October 1996

**Written at the Programme Centre, Norwegian Institute for Water Research**

## SUMMARY

Intercomparison 9610 was organized as a part of the between-laboratory quality control programme, as stated in "Manual for Chemical and Biological Monitoring" (1), by the International Co-operative Programme on Assessment and Monitoring of Acidification in Rivers and Lakes.

The intercomparison was performed in July - August 1996, and included the determination of major ions in natural water samples. The participants were asked to determine pH, conductivity, alkalinity, nitrate + nitrite, chloride, sulfate, calcium, magnesium, sodium, potassium, total aluminium, reactive and non-labile aluminium, dissolved organic carbon and chemical oxygen demand (COD-Mn).

Two sample sets with different concentrations were prepared for this intercomparison, one set for the determination of the major ions and one set for the determination of aluminium fractions and unspecific organic matter. 36 laboratories determined the analytical variables in one or both sample sets.

The samples were sent to 42 laboratories, and 36 submitted results to the Programme Centre before the final statistical treatment of the data submittet by the participants. 21 countries were represented in this laboratory group.

As "true" value for each variable was selected the median value of the results received from the participants. For three analytical variables: alkalinity, reactive and non-labile aluminium, this definition of the " true value" is not acceptable, because of the extreme spread between the results from the different participants. It was therefore decided not to evaluate the reported results for these variables. Excluding these three variables from the evaluation, 70 % of the result pairs were acceptable, the target limit being the median value ± 20 %.

For pH the accuracy limit was extended to ± 0.2 units, and 55 % of the result pairs were included by this special limit. A total error of ± 0.2 units for pH measurements seems to be a more reasonable assessment of the accuracy between laboratories, than the target limit of ± 0.1 units, for samples which are neutral or weakly acid. The reason for the great spread of pH results is mainly due to the fact that different measurement routines are used by the participants.

For sample A there is a lack of agreement between pH and alkalinity, caused by the high concentration of organic anions in this solution. This fact is revealing that the different methods used for the determination of alkalinity are responding differently when bicarbonate no longer is the dominating buffer system in the solution. A sample set with more suitable concentration for alkalinity has to be used in the future.

The best results were reported for conductivity, nitrate + nitrite, calcium, sodium and dissolved organic carbon. Rather poor comparability was observed for pH, alkalinity, chloride and aluminium species. To improve the comparability of the results for these variables, it is necessary to normalize the analytical method and determination technique used.

## CONTENTS

## INTRODUCTION

As stated in "Manual for Chemical and Biological Monitoring" (1), between-laboratory quality control is necessary in multilaboratory programme to assure clear identification and control of the bias between analyses carried out by individual participants of the Programme. Such biases may arise through the use of different analytical methods, errors in the laboratory calibration solutions, or through inadequate within-laboratory control.

The between-laboratory control carried out by the Programme Centre is based on the "round robin" concept and the procedure of Youden (2,3), which is briefly described in Appendix 3. This tenth intercomparison test, called 9610, included the determination of the main components and some other ions in natural water samples: pH, conductivity, alkalinity, nitrate + nitrite, chloride, sulfate, calcium, magnesium, sodium, potassium, total aluminium, reactive and non-labile aluminium, dissolved organic carbon and chemical oxygen demand (COD-Mn).

## ACCOMPLISHMENT OF THE INTERCALIBRATION

The preparation of the sample solutions is described in Appendix 2. The results of the control analyses performed at the Programme Centre are also summarized in the same place. On the Task Force meeting in 1995 it was decided that two sample sets should be included in this intercomparison, one sample pair for the determination of the major ions, and one sample pair for aluminium fractions and unspecific organic matter.

The samples were mailed from the Programme Centre on July 4, 1996. Most of the participating laboratories received the samples within one week, except for some few ones. To ensure that the effect of possible alterations in the solutions is minimized, the participants were asked to analyze the samples as soon as possible, and return the analytical results within six weeks after the samples arrived at the laboratory. As the samples were sent in the summer hollidays time, it was expected that some laboratories might have problems with the time limit for returning the analytical results.

## RESULTS

The samples were sent to 42 laboratories. The 36 boratories who submitted results to the Programme Centre, are representing 21 countries. This time, too, it was a problem that many laboratories submitted the results several weeks after the deadline, and a reminder letter had to be mailed to some of the participants. A survey of the participants and their code numbers are listed in Appendix 1.

The analytical results received from the laboratories were treated by the method of Youden (2,3). A short description of this method, and the statistical treatment of the analytical data, are presented in Appendix 3.

The purpose of this test is to evaluate the comparability of the analytical results produced by different laboratories. The real "true value" is not known exactly for the natural samples used in this intercomparison. Therefore, we selected the median value, determined from the analytical results submitted by the participating laboratories, as the "true value" for each analytical variable. The median value is considered to be an acceptable estimate of the true value for this purpose, as long as the preponderate number of participants are using essentially the same analytical method.

The results are illustrated in Figure 1 - 15, where each laboratory is represented by a small circle and an identification number. The great circle in the figures are representing a selected accuracy limit, either the general target limit of ± 20 % of the mean true values of the sample pair, or a special accuracy limit defined in the sections below. A survey of the results of intercomparison 9610 is presented in Table 1. The individual results of the participants are presented in Table 4 in Appendix 4, sorted in order of increasing identification number. More extensive statistical informations are presented in the Tables 5.1 - 5.15.

## pH

The reported results for pH are graphically presented in Figure 1, where the radius of the great circle is 0.2 pH units, and visualizes the degree of comparability between the pH results from the participating laboratories. The reported pH values are given in Table 5.1 in Appendix 4.

The participating laboratories determined pH in the test solutions by their own routine method. An electrometric method was used by all laboratories. 33 laboratories reported results for pH, of this group 16 indicated that they read the pH value during stirring the solution. As shown in Table 1, there is a small, but systematic difference between the results determined in a quiescent solution, and determined during stirring the solution. For the weakly acid sample A this difference is smaller than for sample B, which is in the circumneutral range. The stirring are lowering the reported pH results.

As the $CO_2$ concentration of samples in the circumneutral range may be far above the atmospheric equilibrium, the relative high $pCO_2$ levels will lead to large systematic errors, the magnitude of which will vary between the laboratories due to different $pCO_2$ levels in the samples caused by different storage and handling conditions. This effect may also increase the random error as the samples may contain different amount of excess $CO_2$. The $CO_2$ effect is obviously far greater in sample B (pH 7) than in sample A (pH 5). This problem is demonstrated by Figure 1, by the far greater spread in the y direction than in the x direction.

The control analyses carried out at the Program Centre proved that the samples were stable when stored within one laboratory. However, the equilibrium of the samples may be influenced by variations in pressure and temperature when they are mailed to the participants. Some systematic deviations observed in Figure 1 may also be due to errors in the instrument, or more likely in the electrodes, as different electrodes may give rise to different results (4). The main reason for the differences in the reported results, however, must be connected to the different measurement methods used by the participants.

**(The text continues on page 24)**

## Table 1. Statistical summary of intercomparison 9610

| Analytical variables and methods | Sample pair | Accepted value 1 | Accepted value 2 | Number of labs. total | Number of labs. omitted | Median 1 | Median 2 | Mean 1 | St.dev. 1 | Mean 2 | St.dev. 2 | Rel. st. dev., % 1 | Rel. st. dev., % 2 | Relative error, % 1 | Relative error, % 2 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| pH | AB | 5.02 | 7.05 | 33 | 0 | 5.02 | 7.05 | 4.98 | 0.15 | 6.98 | 0.24 | 3.1 | 3.5 | -0.9 | -1 |
| No stirring | | | | 17 | 0 | 5.04 | 7.12 | 5 | 0.1 | 7.09 | 0.19 | 2.1 | 2.7 | -0.4 | 0.6 |
| Stirring | | | | 16 | 0 | 4.95 | 6.87 | 4.95 | 0.19 | 6.87 | 0.24 | 3.8 | 3.6 | -1.4 | -2.6 |
| Conductivity | AB | 13.1 | 4 | 32 | 3 | 13.1 | 3.99 | 12.85 | 0.69 | 3.93 | 0.2 | 5.4 | 5.2 | -1.9 | -1.9 |
| Alkalinity | AB | 20.4 | 11 | 27 | 18 | 20.4 | 11 | 18.51 | 5.16 | 11.33 | 0.87 | 27.9 | 7.7 | -9.2 | 3 |
| Gran plot titration | | | | 8 | 5 | 20.4 | 10.7 | 18.53 | 4.69 | 10.7 | 0.3 | 25.3 | 2.8 | -9.2 | 2.7 |
| End point titration | | | | 9 | 6 | 12.5 | 10.7 | 14.43 | 5.08 | 11.33 | 1.27 | 35.2 | 11.2 | -9.2 | 3 |
| End point 5.6 | | | | 1 | 1 | | | -26.2 | | 9.8 | | | | -228 | -11 |
| End point 5.4 | | | | 2 | 2 | | | | | 12.65 | | | | -585 | 15 |
| End point 4.5 or 4.2 | | | | 4 | 1 | | | 23.57 | | 11.82 | | | | 15.5 | 7.4 |
| Colorimetry | | | | 1 | 1 | | | 32 | | 14.5 | | | | 57 | 32 |
| Not documented | | | | 2 | 2 | | | -10.72 | | 11.62 | | | | -152 | 5.6 |
| Nitrate + nitrite-nitrogen | AB | 160 | 187 | 33 | 3 | 160 | 187 | 161 | 13 | 184 | 14 | 8.1 | 7.8 | 0.9 | -1.8 |
| Autoanalyzer | | | | 10 | 0 | 159 | 187 | 160 | 12 | 187 | 19 | 7.8 | 9.9 | -0.1 | 0.3 |
| Photometry | | | | 5 | 1 | 160 | 189 | 165 | 17 | 190 | 10 | 10.6 | 5.2 | 3 | 1.3 |
| Ion chromatography | | | | 15 | 2 | 160 | 187 | 162 | 14 | 180 | 13 | 8.8 | 7.1 | 1.1 | -3.6 |
| Flow injection anal. | | | | 1 | 0 | | | 156 | | 181 | | | | -2.5 | -3.2 |
| Hydrazine method | | | | 1 | 0 | | | 155 | | 170 | | | | -3.1 | -9.1 |
| Photometry | | | | 1 | 1 | | | 2490 | | 3058 | | | | ** | ** |
| Cap. electrophoresis | | | | 1 | 0 | | | 171 | | 181 | | | | 6.9 | -3.2 |
| Chloride | AB | 0.7 | 1.45 | 32 | 12 | 0.7 | 1.45 | 0.67 | 0.14 | 1.45 | 0.09 | 21.7 | 6.5 | -4.8 | 0.2 |
| Ion chromatography | | | | 25 | 9 | 0.68 | 1.47 | 0.66 | 0.14 | 1.45 | 0.07 | 20.7 | 5.1 | -5.7 | -0.1 |
| Photometry, automated | | | | 2 | 0 | | | 0.67 | | 1.5 | | | | -5 | 3.4 |
| Argentometry | | | | 1 | 1 | | | 12.78 | | 17.75 | | | | ** | ** |
| Manual, Hg | | | | 3 | 2 | | | 0.7 | | 1.44 | | | | 0 | -0.7 |

| Analytical variables and methods | Sample pair | Accepted value 1 | Accepted value 2 | Number of labs. total | Number of labs. omitted | Median 1 | Median 2 | Mean 1 | St.dev. | Mean 2 | St.dev. | Relative st. dev., 1 | Relative st. dev., 2 | Relative error, % 1 | Relative error, % 2 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sulfate | AB | 2.77 | 3.67 | 32 | 2 | 2.77 | 3.67 | 2.77 | 0.38 | 3.66 | 0.34 | 13.6 | 9.2 | 0.2 | -0.4 |
| Ion chromatography | | | | 26 | 1 | 2.76 | 3.67 | 2.76 | 0.36 | 3.63 | 0.34 | 12.9 | 9.5 | -0.5 | -1.1 |
| Photometry | | | | 1 | 0 | | | 2.7 | | 3.6 | | | | -2.5 | -1.9 |
| Nephelometry | | | | 2 | 1 | | | 2.2 | | 3.6 | | | | -20.6 | -1.9 |
| ICP | | | | 2 | 0 | | | 3.21 | | 4.03 | | | | 15.9 | 9.8 |
| Cap. electrophoresis | | | | 1 | 0 | | | 3.02 | | 3.69 | | | | 9 | 0.5 |
| Calcium | AB | 1.5 | 5.3 | 32 | 2 | 1.5 | 5.3 | 1.49 | 0.23 | 5.22 | 0.36 | 15.6 | 6.8 | -1 | -1.5 |
| FAAS | | | | 14 | 0 | 1.49 | 5.31 | 1.46 | 0.25 | 5.21 | 0.37 | 16.9 | 7.2 | -2.9 | -1.8 |
| ICP | | | | 9 | 1 | 1.55 | 5.33 | 1.59 | 0.22 | 5.34 | 0.21 | 14 | 3.9 | 5.9 | 0.7 |
| EDTA | | | | 2 | 1 | | | 1.62 | | 4.45 | | | | 8 | -16 |
| Ion chromatography | | | | 6 | 0 | 1.46 | 5.31 | 1.41 | 0.23 | 5.32 | 0.33 | 16.3 | 6.3 | -6.2 | 0.3 |
| ICP-MS | | | | 1 | 0 | | | 1.4 | | 4.7 | | | | -6.7 | -11.3 |
| Magnesium | AB | 0.2 | 0.44 | 32 | 5 | 0.2 | 0.44 | 0.19 | 0.01 | 0.44 | 0.03 | 6.8 | 6.7 | -3.2 | -1.1 |
| FAAS | | | | 14 | 1 | 0.2 | 0.44 | 0.19 | 0.01 | 0.43 | 0.03 | 4.9 | 7.7 | -4 | -2.6 |
| ICP | | | | 9 | 2 | 0.2 | 0.45 | 0.19 | 0.01 | 0.44 | 0.03 | 7.6 | 6.9 | -4.3 | 1.1 |
| EDTA | | | | 2 | 2 | | | 0.43 | | 1.4 | | | | 115 | 218 |
| Ion chromatography | | | | 6 | 0 | 0.2 | 0.44 | 0.2 | 0.02 | 0.45 | 0.01 | 9.8 | 1.9 | -0.8 | 1.1 |
| ICP-MS | | | | 1 | 0 | | | 0.2 | | 0.4 | | | | 0 | -9.1 |
| Sodium | AB | 0.89 | 1.3 | 33 | 1 | 0.89 | 1.3 | 0.92 | 0.11 | 1.3 | 0.11 | 11.8 | 8.3 | 3.8 | 0.2 |
| FAAS | | | | 12 | 0 | 0.89 | 1.28 | 0.89 | 0.09 | 1.27 | 0.1 | 10.3 | 7.5 | -0.6 | -2.2 |
| ICP | | | | 9 | 0 | 0.91 | 1.3 | 0.97 | 0.15 | 1.34 | 0.13 | 15.1 | 9.9 | 8.8 | 2.7 |
| AES | | | | 6 | 1 | 0.98 | 1.3 | 0.96 | 0.11 | 1.34 | 0.15 | 11 | 10.9 | 8 | 3.4 |
| Ion chromatography | | | | 5 | 0 | 0.88 | 1.28 | 0.88 | 0.01 | 1.27 | 0.02 | 1.3 | 1.9 | -0.7 | -2 |
| ICP-MS | | | | 1 | 0 | | | 1 | | 1.3 | | | | 12.4 | 0 |
| Potassium | AB | 0.22 | 0.32 | 33 | 6 | 0.22 | 0.32 | 0.22 | 0.03 | 0.32 | 0.04 | 14.5 | 13.1 | 1.4 | 0 |
| FAAS | | | | 12 | 0 | 0.23 | 0.33 | 0.23 | 0.02 | 0.32 | 0.03 | 8.3 | 10.2 | 3.6 | 0 |
| ICP | | | | 9 | 4 | 0.22 | 0.35 | 0.22 | 0.03 | 0.34 | 0.04 | 12.5 | 11 | -1.8 | 7.5 |
| AES | | | | 6 | 1 | 0.22 | 0.3 | 0.21 | 0.02 | 0.3 | 0.02 | 8.6 | 6.2 | -5.5 | -6.2 |
| Ion chromatography | | | | 5 | 1 | 0.22 | 0.32 | 0.22 | 0.06 | 0.3 | 0.07 | 28.4 | 22.6 | -1.1 | -7.8 |
| ICP-MS | | | | 1 | 0 | | | 0.3 | | 0.4 | | | | 36.4 | 25 |

| Analytical variables and methods | Sample pair | Accepted value 1 | Accepted value 2 | Number of labs. total | Number of labs. omitted | Median 1 | Median 2 | Mean 1 | St.dev. | Mean 2 | St.dev. | Relative st. dev., 1 | Relative st. dev., 2 | Relative error, % 1 | Relative error, % 2 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Aluminium | CD | 82 | 114 | 17 | 0 | 82 | 114 | 82 | 21 | 111 | 19 | 25.1 | 17 | -0.3 | -2.4 |
| GFAAS | | | | 4 | 0 | 78 | 114 | 75 | 19 | 101 | 28 | 25.3 | 27.6 | -8.6 | -11.1 |
| ICP | | | | 7 | 0 | 82 | 111 | 80 | 18 | 111 | 13 | 23 | 11.3 | -2.3 | -2.2 |
| ICP-MS | | | | 3 | 0 | 90 | 116 | 99 | 21 | 125 | 17 | 20.9 | 13.7 | 20.4 | 10 |
| Photometry | | | | 3 | 0 | 82 | 104 | 78 | 29 | 110 | 21 | 37 | 18.8 | -5.3 | -3.6 |
| Aluminium, reactive | CD | 24 | 99 | 9 | 5 | 24 | 99 | 24 | 3 | 100 | 10 | 12.1 | 9.6 | -1.7 | 0.6 |
| Photometry, PCV | | | | 7 | 4 | 25 | 105 | 24 | 3 | 102 | 10 | 14.5 | 10.3 | -0.8 | 2.8 |
| Photometry, BPR | | | | 1 | 0 | | | 23 | | 93 | | | | -4.2 | -6.1 |
| ICP | | | | 1 | 1 | | | 80 | | 150 | | | | 233.3 | 51.5 |
| Aluminium, nonlabile | CD | 50 | 21 | 8 | 4 | 50 | 21 | 48 | 9 | 21 | 6 | 19.2 | 27 | -4 | 1.2 |
| Photometry, PCV | | | | 6 | 3 | 46 | 24 | 45 | 9 | 23 | 6 | 19 | 27 | -10 | 7.9 |
| Photometry, BPR | | | | 1 | 1 | | | 54 | | 43 | | | | 8 | 104.8 |
| ICP | | | | 1 | 0 | | | 57 | | 17 | | | | 14 | -19 |
| Dissolved org. carbon | CD | 3.72 | 3.25 | 13 | 0 | 3.72 | 3.25 | 3.89 | 0.48 | 3.36 | 0.34 | 12.4 | 10 | 4.6 | 3.5 |
| Combustion | | | | 6 | 0 | 3.8 | 3.3 | 3.73 | 0.2 | 3.26 | 0.14 | 5.3 | 4.2 | 0.4 | 0.2 |
| UV/S2O8 | | | | 5 | 0 | 4.22 | 3.49 | 4.24 | 0.63 | 3.59 | 0.45 | 14.8 | 12.5 | 13.9 | 10.5 |
| Phenolphthalein | | | | 2 | 0 | | | 3.51 | | 3.12 | | | | -5.6 | -4 |
| Chem. oxygen demand | CD | 4 | 3.22 | 6 | 1 | 4 | 3.22 | 4.33 | 0.83 | 3.2 | 0.21 | 19.2 | 6.6 | 8.2 | -0.5 |

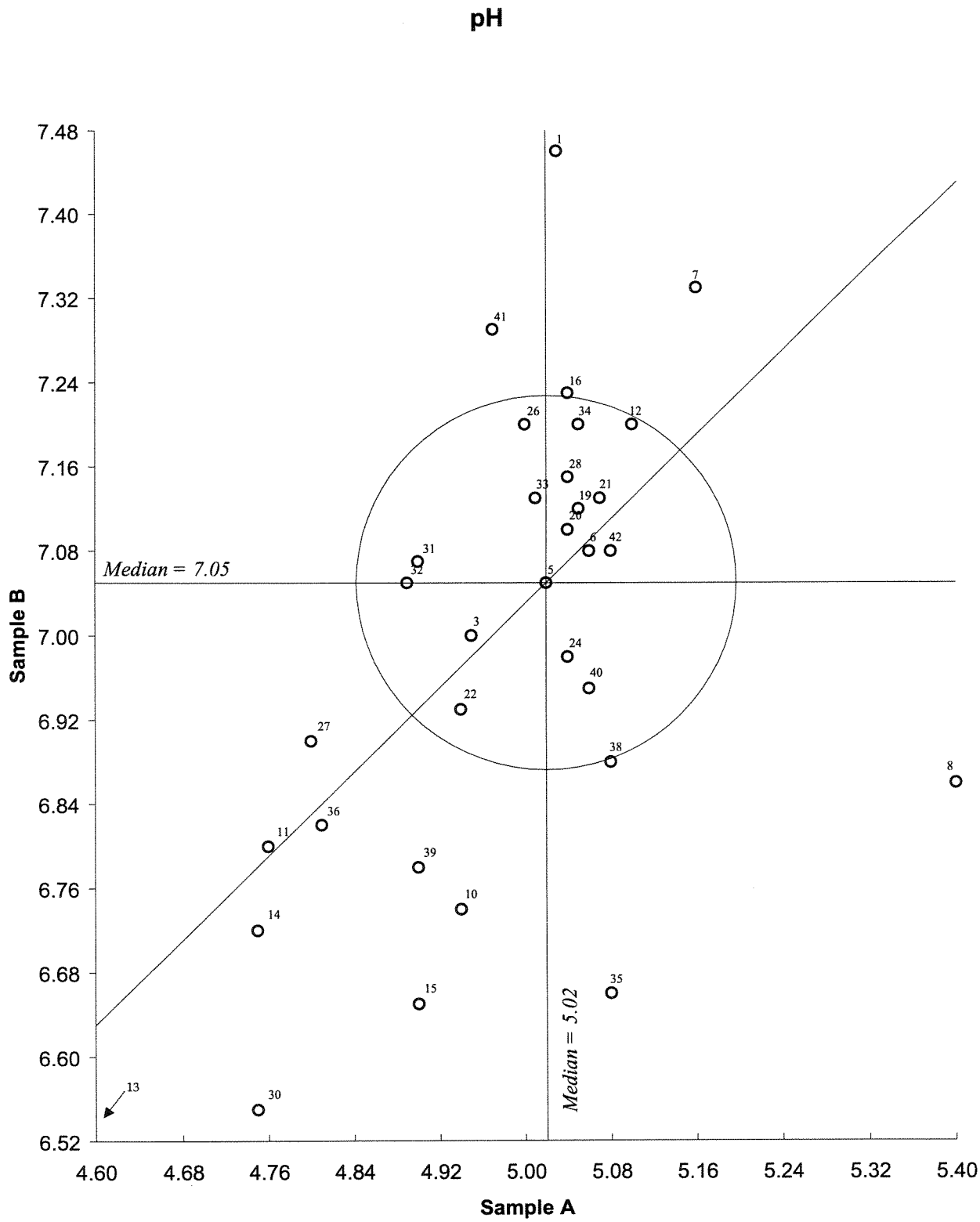


Figure 1. Youden-diagramme for pH, Pair AB
Acceptance criterium, given by the circle, is 0.2 pH units

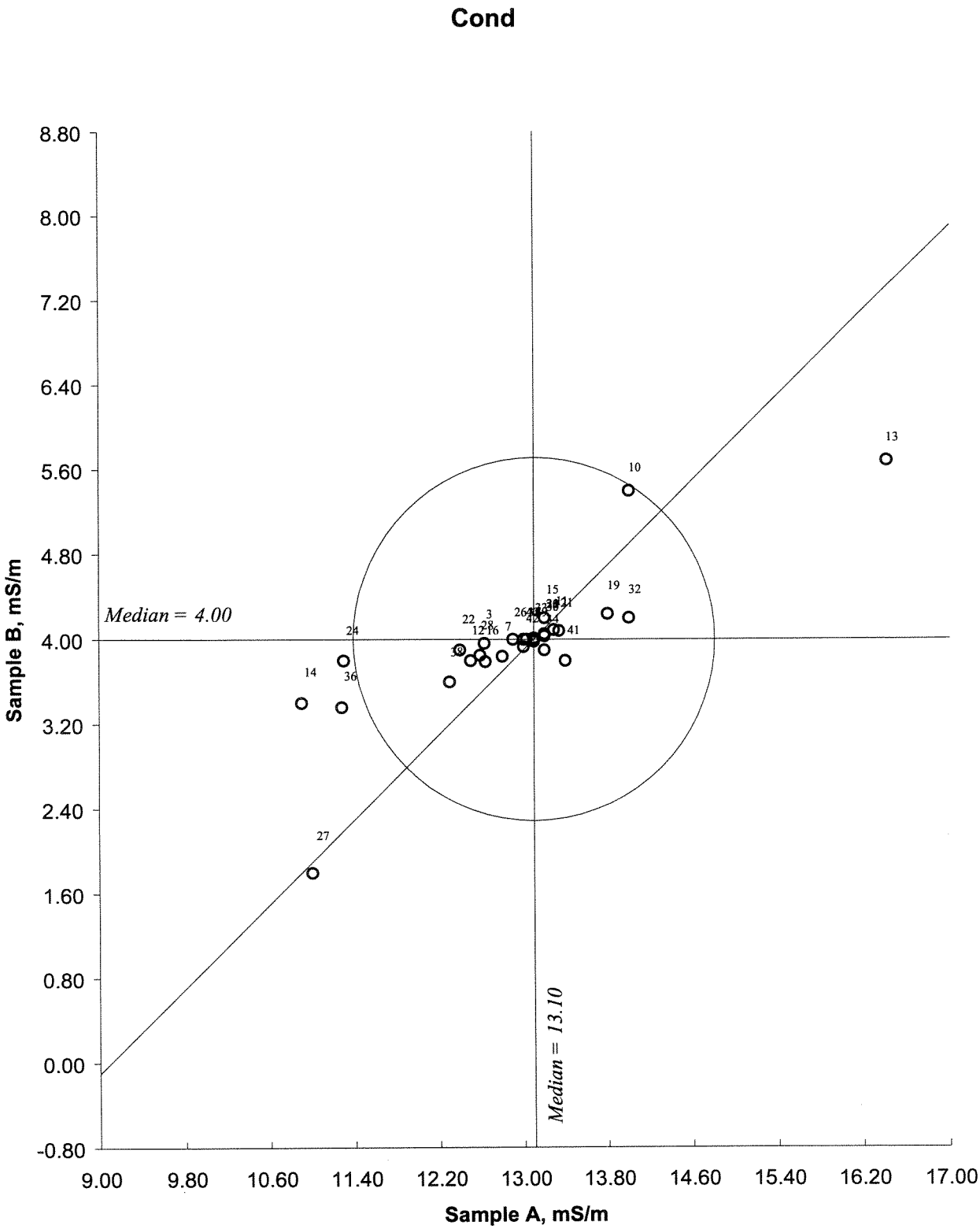


Figure 2. Youden-diagramme for conductivity, Pair AB
Acceptance criterium, given by the circle, is 20 %

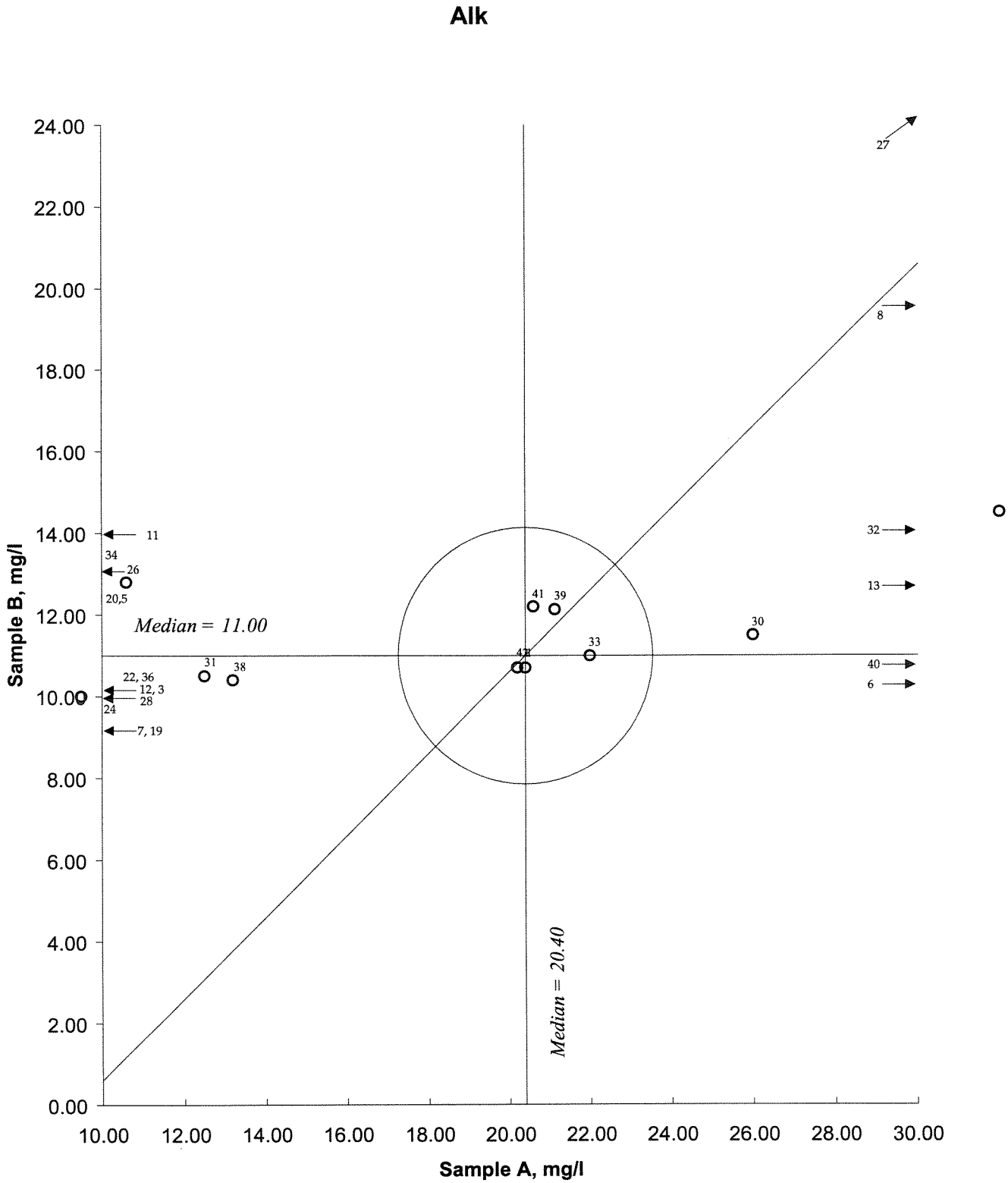


Figure 3. Youden-diagramme for alkalinity, Pair AB
Acceptance criterium, given by the circle, is 20 %

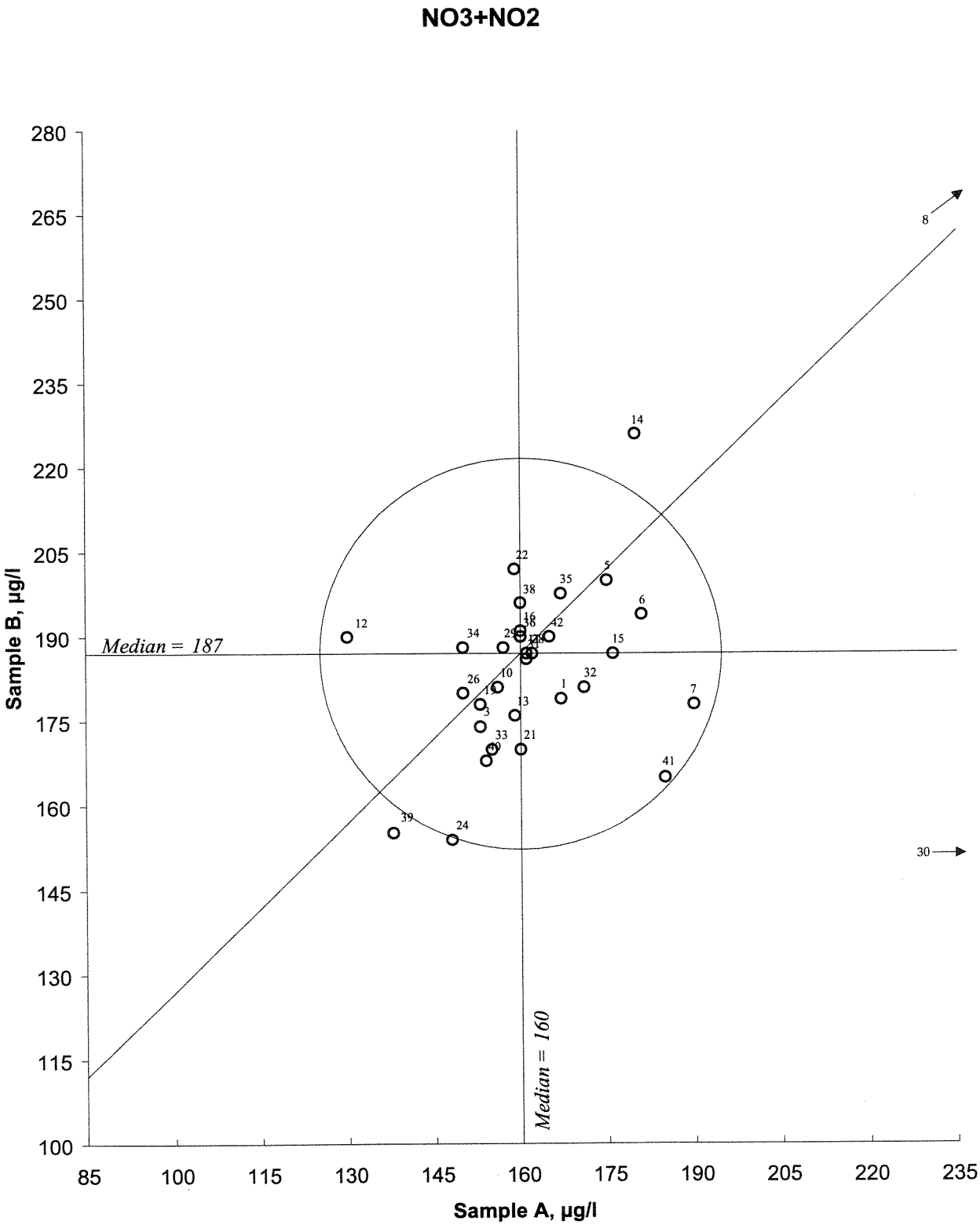


Figure 4. Youden-diagramme for nitrate + nitrite-nitrogen, Pair AB
Acceptance criterium, given by the circle, is 20 %

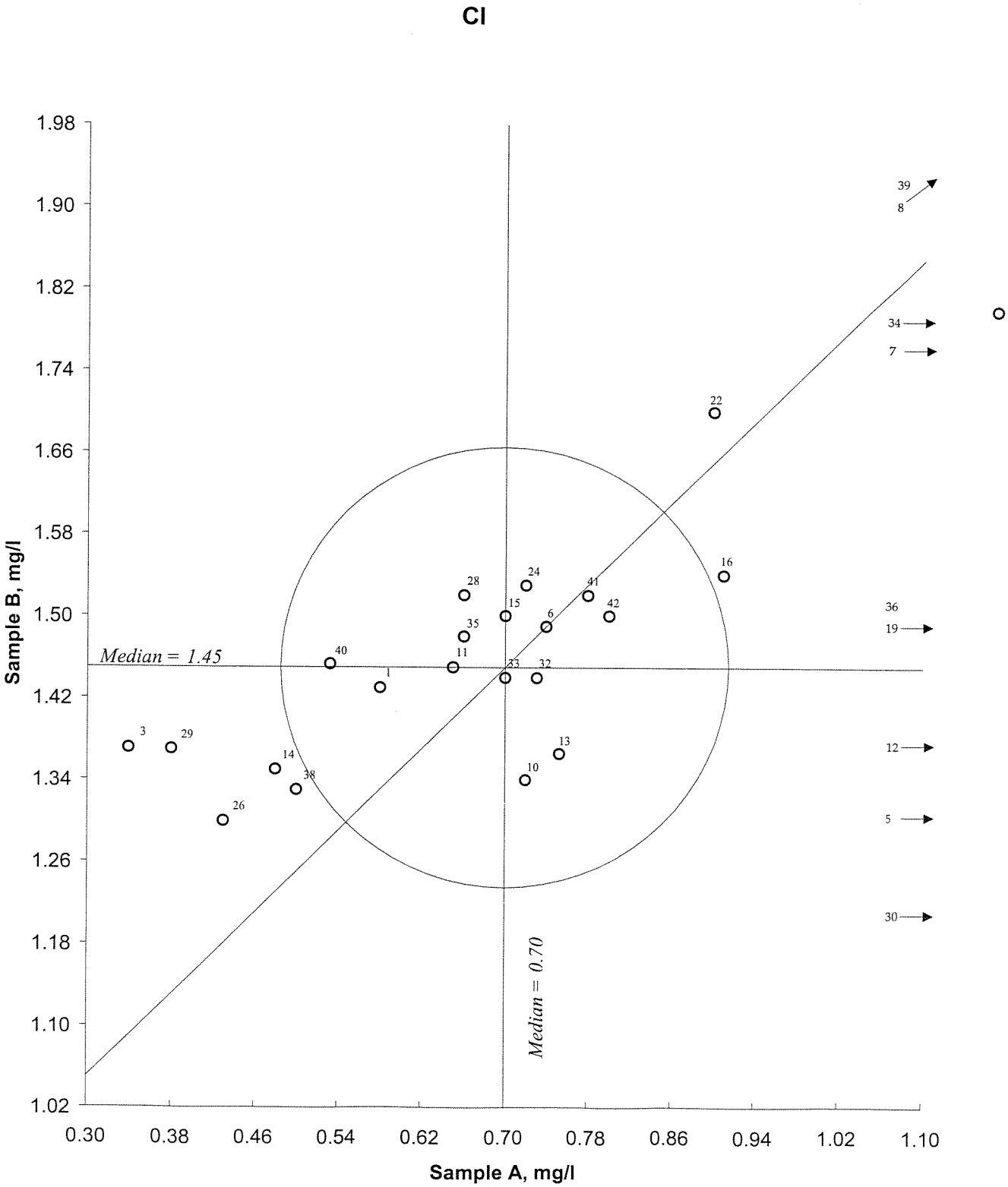


Figure 5. Youden-diagramme for chloride, Pair AB
Acceptance criterium, given by the circle, is 20 %

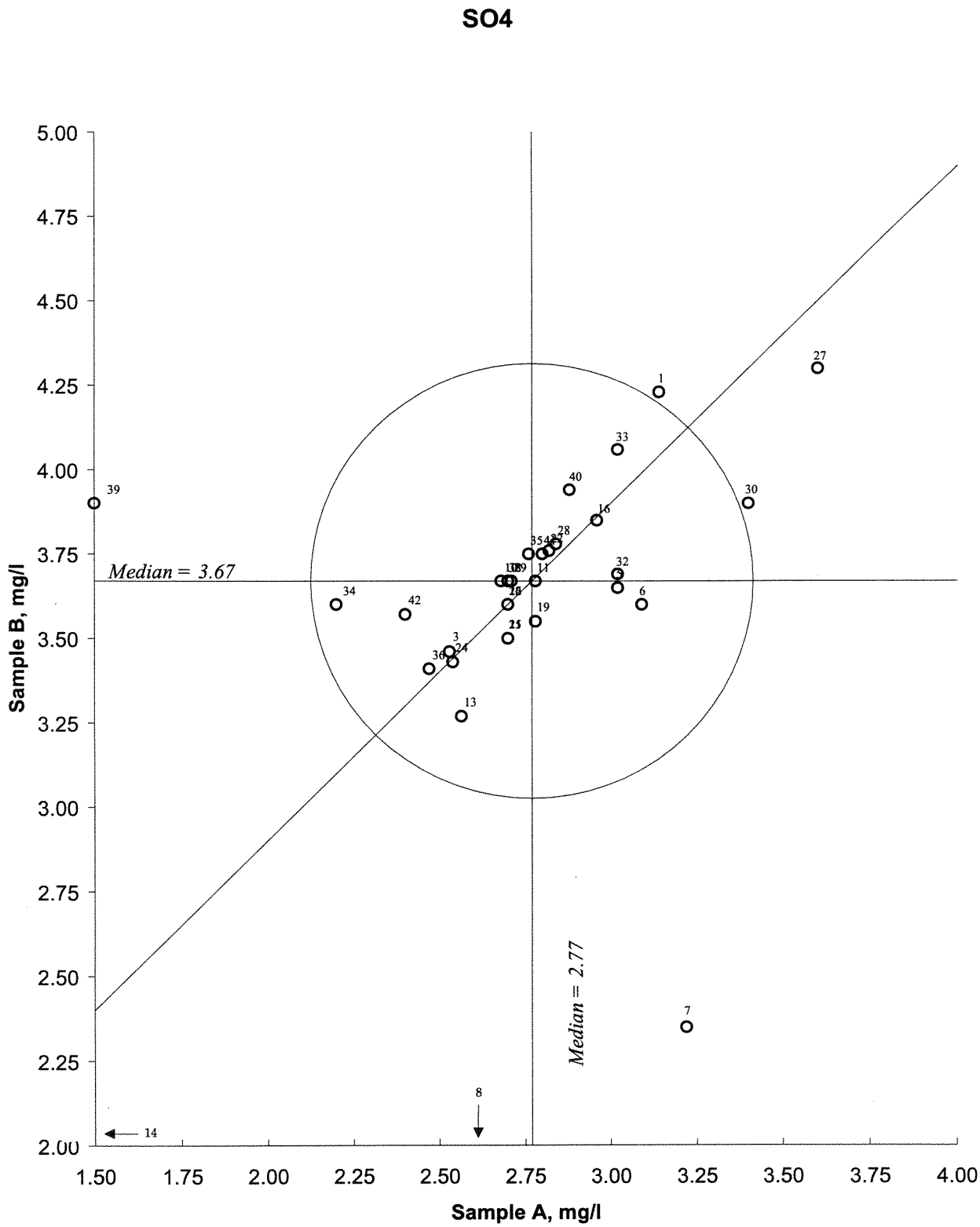


Figure 6. Youden-diagramme for sulfate, Pair AB
Acceptance criterium, given by the circle, is 20 %

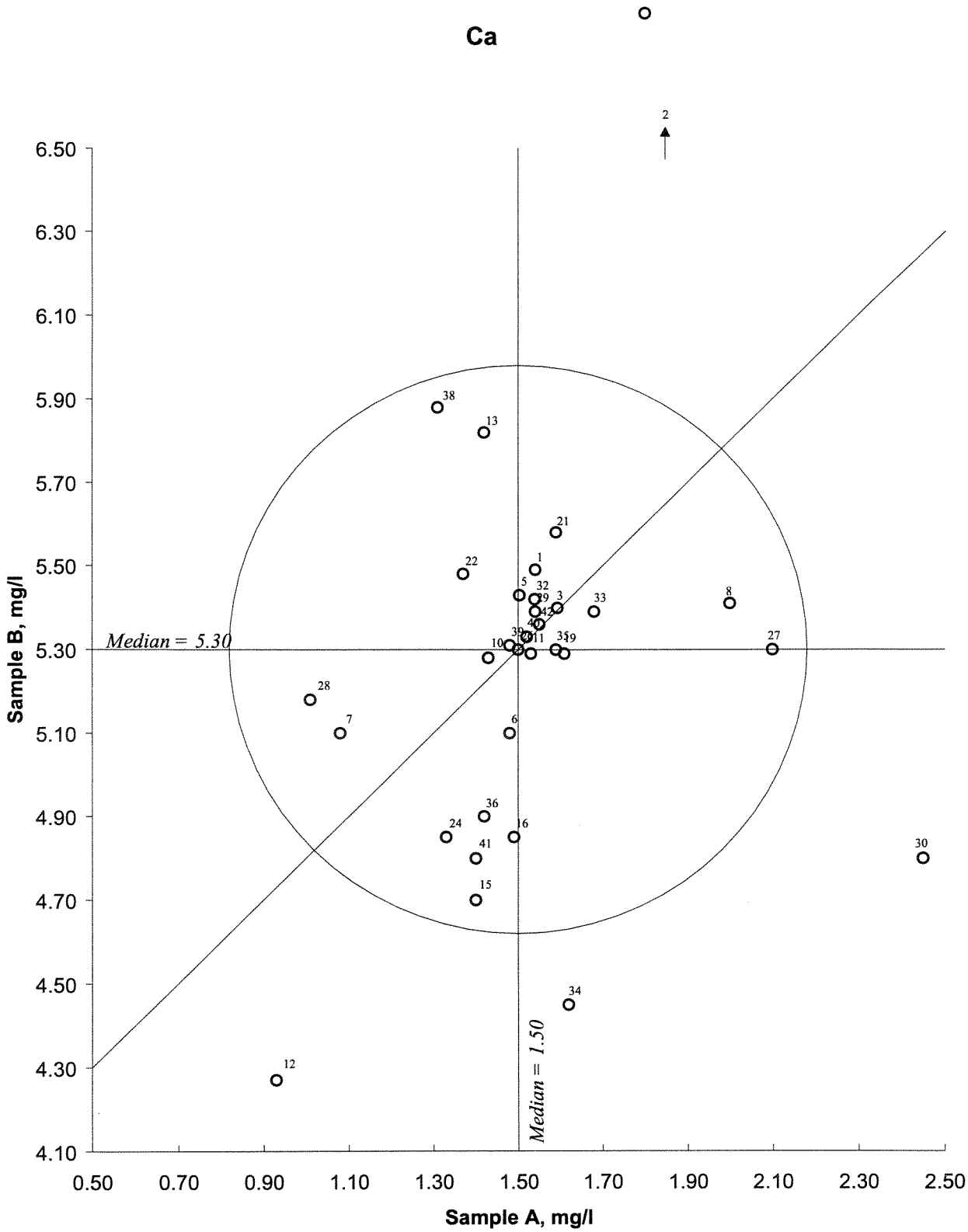


Figure 7. Youden-diagramme for calcium, Pair AB
Acceptance criterium, given by the circle, is 20 %

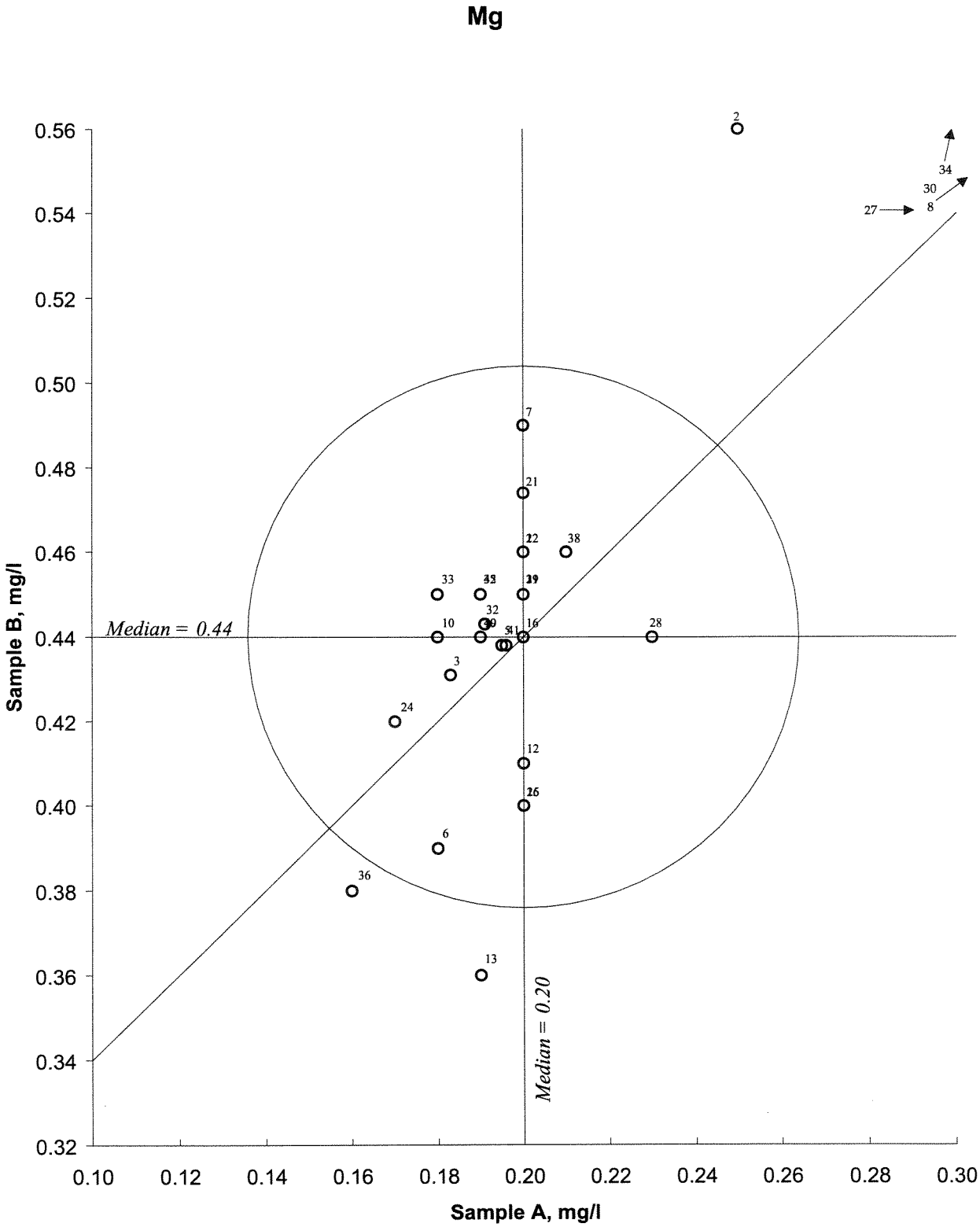


Figure 8. Youden-diagramme for magnesium, Pair AB
Acceptance criterium, given by the circle, is 20 %

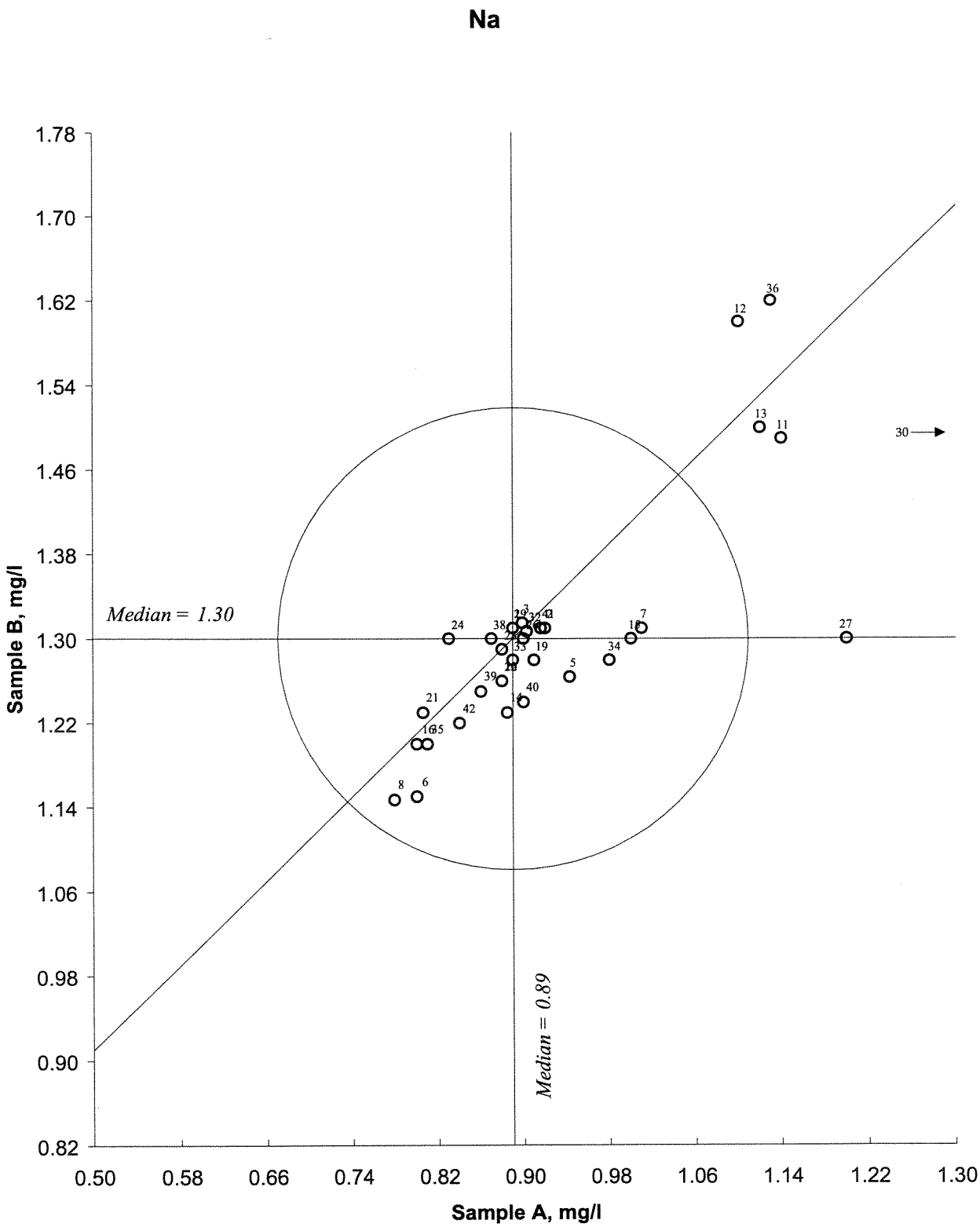


Figure 9. Youden-diagramme for sodium, Pair AB
Acceptance criterium, given by the circle, is 20 %

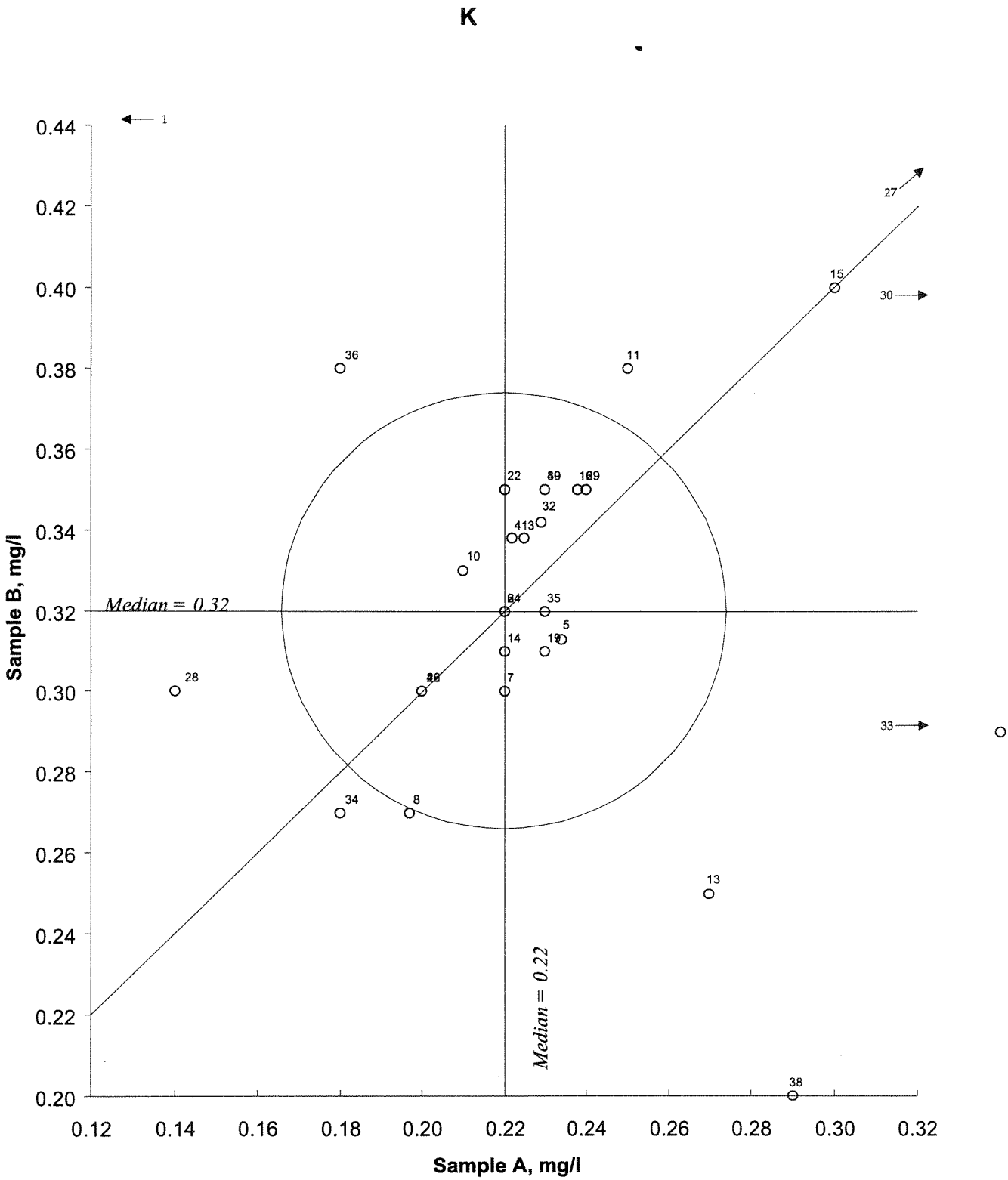


Figure 10. Youden-diagramme for potassium, Pair AB
Acceptance criterium, given by the circle, is 20 %

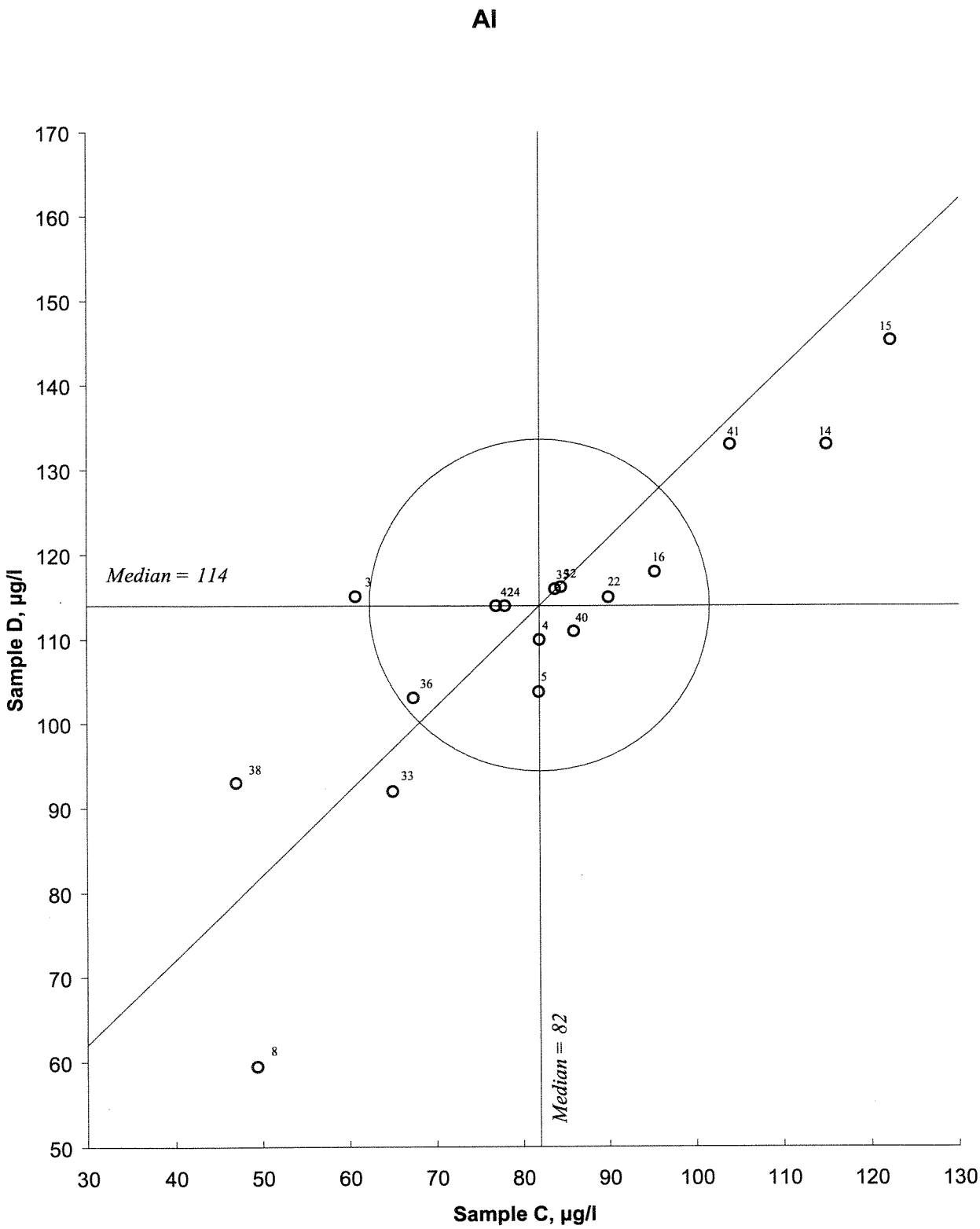


Figure 11. Youden-diagramme for aluminium, Pair CD
Acceptance criterium, given by the circle, is 20 %

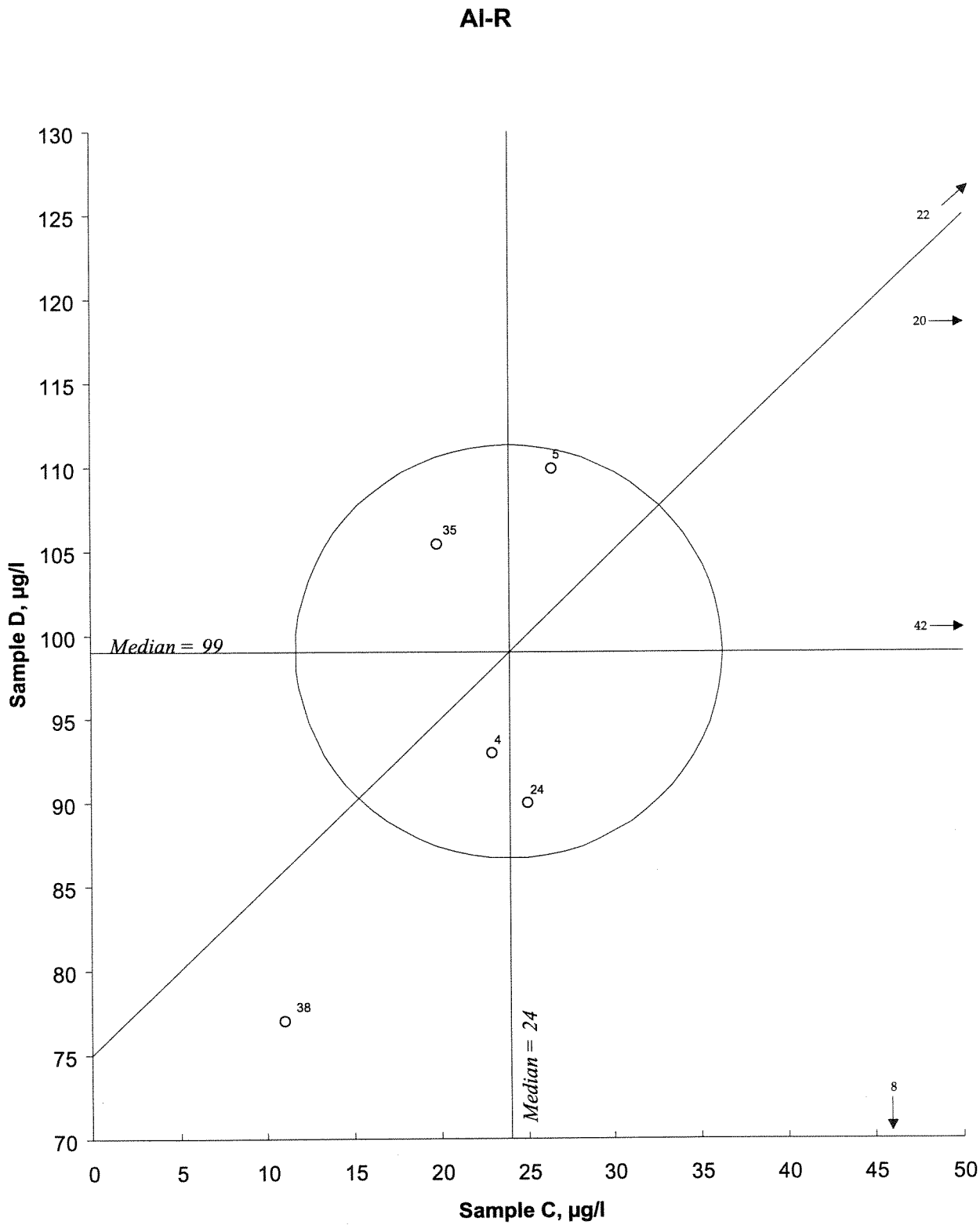


Figure 12. Youden-diagramme for aluminium, reactive, Pair CD
Acceptance criterium, given by the circle, is 20 %

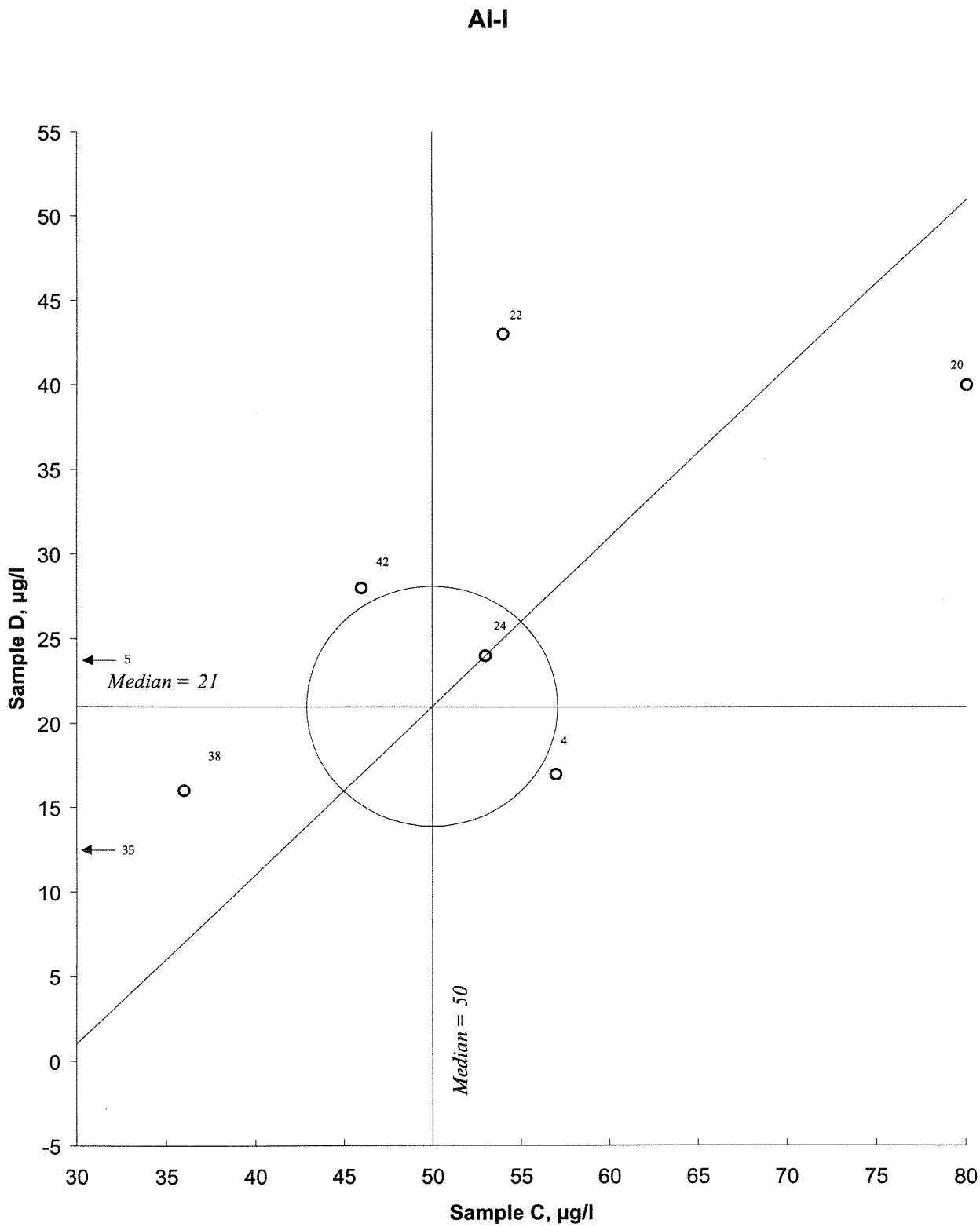


Figure 13. Youden-diagramme for aluminium, nonlabile, Pair CD
Acceptance criterium, given by the circle, is 20 %

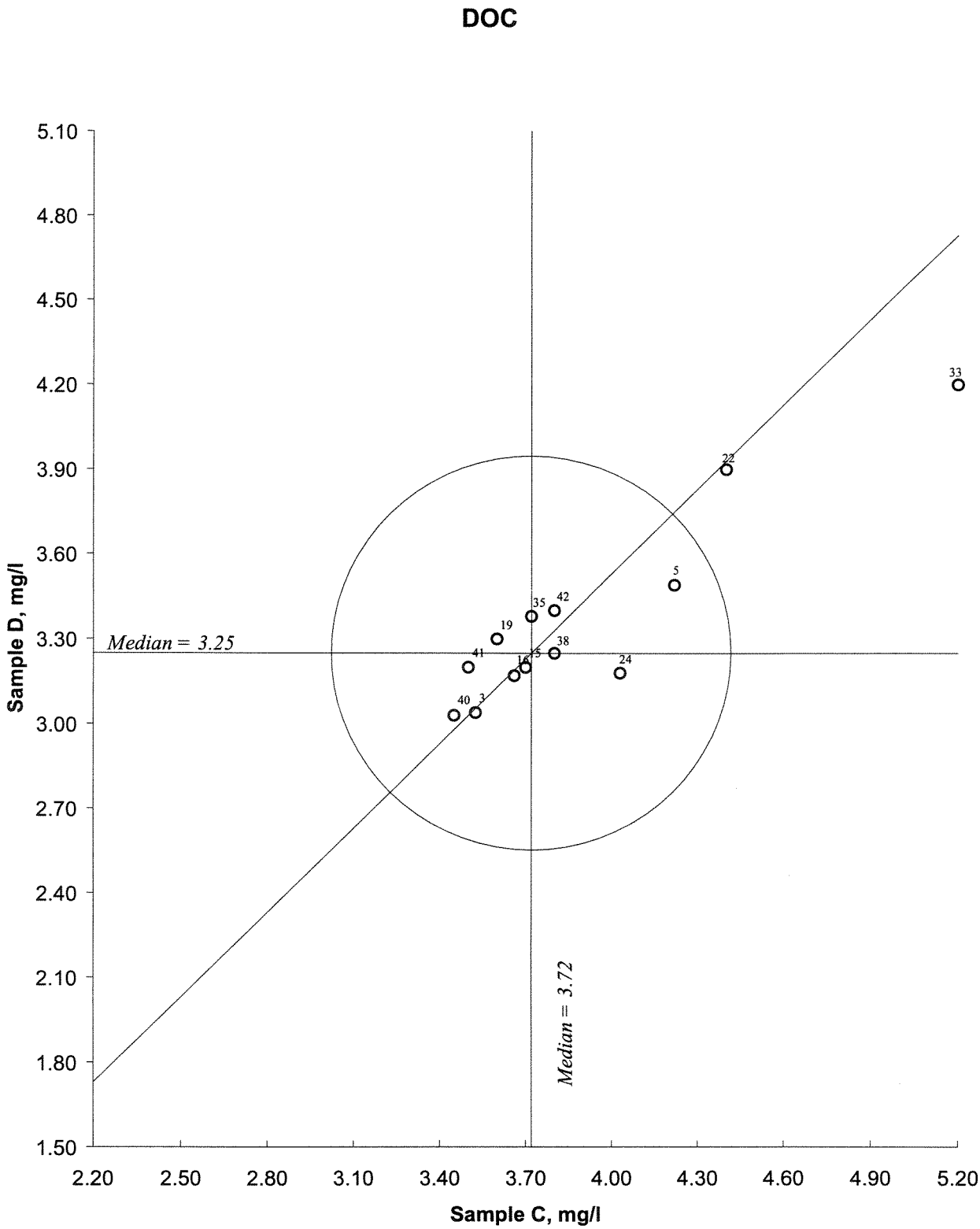


Figure 14. Youden-diagramme for dissolved organic carbon, Pair CD
Acceptance criterium, given by the circle, is 20 %

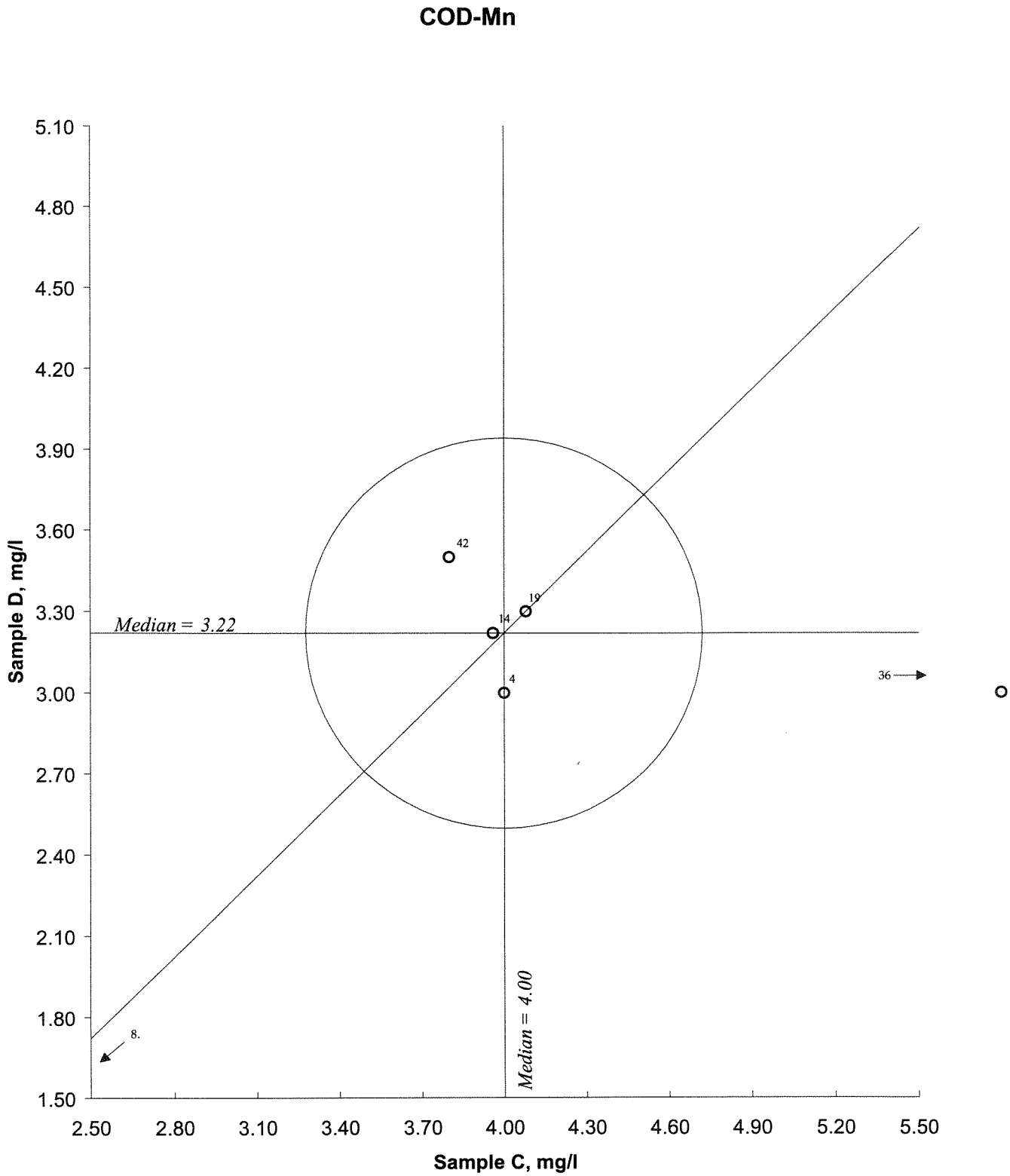


Figure 15. Youden-diagramme for chemical oxygen demand, Pair CD
Acceptance criterium, given by the circle, is 20 %

## Conductivity

The conductivity results are presented in Figure 2, where the great circle is representing an accuracy limit of ± 20 %. The reported results are given in Table 5.2 in Appendix 4. Some laboratories reported the conductivity results in the unit µS/cm, which they use routinely, instead of the requested mS/m at 25 °C. Therefore, some correspondance with these laboratories was necessary to clarify the results, which were recalculated to mS/cm. All participants used an electrometric method for the determination of conductivity.

Most laboratories achieved good agreement between the results for this variable. One laboratory reported results being systematically too high for both the samples, and four laboratories reported results being systematically too low and also influenced by random error. Only one more result would be located outside the acceptance limit if the general target accuracy is reduced from ± 20 % to ± 10 %.

## Alkalinity

The alkalinity results are illustrated in Figure 3, and the reported results are given in Table 5.3 in Appendix 4. Roughly one third of the laboratories used the Gran plot titration method suggested in the Manual (1). The others used end point titration, either to pH 4.5 and 4.2, or to one given pH value only (4.2, 4,5, 5.4, or 5.6).

There is a very wide spread of the results for alkalinity at this intercomparison, and this is mainly due to sample A. This sample is deviating from " normal" surface water because acetic acid was added to lower pH of the solution. Therefore there is a very high concentration of organic anions in the solution, and consequently there is no clear connection between pH and alkalinity. The methods used for the determination of alkalinity are usually based on the assumption that the bicarbonate system is the dominating buffer in normal surface waters. When a buffer system with maximum capacity at another pH than bicarbonate is dominating the solution, the different methods may give rise to deviating results.

It has obviously been confusing for many of the participants that there is a lack of connection between pH and alkalinity, and therefore, the alkalinity results in this intercomparison can hardly be evaluated in the traditional way. Because of the the different methods used by the participants, we are not able to estimate a " correct" value for alkalinity in this situation. The " true" value in Figure 3 has therefore to be considered as an arbitrary one only, even when it is calculated in the usual statistical way.

Figure 3 demonstrates quite clearly that it is not possible to evaluate the results for alkalinity in this intercomparison. Table 5.3 demonstrate that the spread of alkalinity results is far greater for sample A than for sample B. A closer investigation of the results shows that laboratories using the same method normally have achieved comparable results. Sample B is what we may call a " normal" water sample, and nearly all the laboratories have reported comparable results - only four laboratories have reported results being systematically too high.

The alkalinity value may vary significantly with the end-point pH used for the titration. In waters containing high concentrations of total inorganic carbon, the equivalence point is close to pH = 5.4. In this case, the relative error introduced by assuming a fixed end-point pH, is negligible. However, at lower alkalinities normally encountered in areas sensitive to acidification, the "total fixed end-point method" overestimates the true alkalinity or the "equivalence" alkalinity.

**Nitrate + nitrite**

The results reported for this parameter are presented in Figure 4, and the reported results are given in Table 5.4 in Appendix 4. Ion chromatography is used by an increasing number of laboratories, and is now used by nearly 50 % of the participants. The others are determining this analytical variable by photometric methods, most of these laboratories are using an automated method. There is no significant difference between the results determined by the principally different methods. However, some few strongly deviating results are determined by manual methods. One laboratory used a method with too high detection limit.

The circle in Figure 4 is representing a general target accuracy of ± 20 %.

**Chloride**

The chloride results are presented in Figure 5, and the reported results from the participants are given in Table 5 (Appendix 4). 25 out of 32 laboratories determined chloride by ion chromatography. In addition, three laboratories used photometric determination with the mercury thiocyanate method, and most of these laboratories used an automated version of the method. The greatest deviations are observed for the manual photometric methods, and especially the argentomertic method which have too high detection limit, the method being too less sensitive for this kind of samples.

For chloride there is observed a rather great difference in quality of the results for sample A and sample B. The spread of the reported results for sample B is far less than for sample A, thus 84 % of the results for sample B alone are acceptable, while only 41 % results for sample A alone are acceptable. A few of the participants reported that they had some problems with the ion chromatography method for chloride, and it is quite probable that the high content of organic anions in sample A may be due to the problems.

**Sulfate**

The sulfate results are illustrated in Figure 6, and the reported values are given in Table 5.6 (Appendix 4). Ion chromatography is used by 26 of 32 laboratories for the determination of this analytical variable. One laboratory used an automated photometric method based on the dissociation of the barium-thorin complex, and two laboratories used a nephelometric method. Two laboratories determined sulfate as total sulfur by ICP, and one laboratory used capillary chromatography with acceptable results.

An accuracy limit of ± 20 % is represented by the circle in Figure 6, and 75 % of the result pairs are located within this general target accuracy. The strongly deviating results are mainly determined by manual photometric or turbidimetric methods. One laboratory reported results strongly affected by random errors.

**Calcium**

The calcium results are illustrated in Figure 7, and the reported values are given in Table 5.7 in Appendix 4. Twelve of the participants used flame atomic absorption spectrometry for the determination of calcium. ICP and ICP-MS techniques, and ion chromatography, are used by nine, one and six laboratories, respectively. The complexometric titration method used by two laboratories is not sensitive enough for this kind of samples.

**Magnesium**

The magnesium results are presented in Figure 8, and the reported values are given in Table 5.8 in Appendix 4. Most of the participants are still using flame atomic absorption spectrometry for the determination of magnesium. Different ICP emission spectrometry techniques and ion chromatography was used by ten and six laboratories, respectively. Systematic deviations are dominating the results outside the target accuracy of ± 20 %, and the greatest deviations are observed for manual titrations, indicating that the concentrations of the samples used in this intercomparison are too low for this technique.

**Sodium**

The sodium results are presented in Figure 9, where the great circle is representing the general target accuracy of ± 20 %. The reported values are given in Table 5.9 (Appendix 4). Most laboratories used flame atomic absorption spectrometry for this determination, however, in many laboratories the emission spectrometric techniques are slowly taking over the routine determinations, thus nine participants used ICP, one ICP-MS and six flame photometry.

82 % of the result pairs are located within the general target accuracy of ± 20 %. Five laboratories reported results which are systematically high, and one where the deviations are of random nature.

**Potassium**

The potassium results are presented in Figure 10. The great circle is representing a general acceptance limit of ± 20 %. The reported values are given in Table 5.10 in Appendix 4. As for sodium, most laboratories used flame atomic absorption spectrometry for the determination of this element, however, emission spectrometry is used by some of the laboratories. The deviations are mainly of systematic nature, however, for some laboratories the deviations are quite random. Two laboratories using ICP had too high detection limit to determine potassium in these samples.

**Total aluminium**

The results for total aluminium are illustrated in Figure 11, and the reported values are given in Table 5.11 (Appendix 4). The great circle is representing the general accuracy target of ± 20 %. Most laboratories are now using emission techniques for the determination of aluminium.

79 % of the result pairs are located within the target accuracy. Three of the deviating results are probably affected by random errors. Only three of the laboratories reported results using photometric methods (autoanalyzer), the other laboratories used atomic absorption or ICP techniques. The dominating error is systematic, both for the very high and very low results.

**Reactive aluminium**

The results for reactive aluminium are illustrated in Figure 12, and the reported values are given in Table 5.12 (Appendix 4). Only nine laboratories reported results for reactive aluminium. The statistical treatment according to Youden, leads to the exclusion of five laboratories. One of the excluded results are systematically low, while the other four were too high. The median value used as a picture of the "true" value, therefore, has to be considered as indicative only.

The reported values for this aluminium fraction are strongly dependent on the chemical conditions in the reaction mixture. Most methods are based on the direct determination of aluminium in a non-acidified sample, preferably accomplished as soon as possible after sampling. By these methods acid is added as a part of the determination step. However, there are some methods based on acid pretreatment of the sample, then the results are dependent on how long time the acidified samples have been stored before the aluminium content is determined. Such acidification is no digestion, but will lead to dissolution of complexes and even dissolution of some particulate matter containing aluminium. The results are expected to increase towards an upper limit when the pretreatment time is prolonged.

**Non-labile aluminium**

The results for non-labile aluminium are illustrated in Figure 13, and the reported values are given in Table 5.13 (Appendix 4). Four of the eight result pairs were excluded by the statistical treatment of the data, because of the great spread in the reported analytical values. Most laboratories have indicated that they determined non-labile aluminium according to the automated method of Røgeberg and Henriksen (6), which is based on the method of Driscoll (7). By this method non-labile aluminium is the fraction that passes through a cation exchange column, and consists of monomeric alumino-organic complexes (see Figure 18, page 42). Some of the informations given by the participants indicate that different resin forms have been used for this intercomparison, and it is well known that different resins have different exchange properties, and will affect the results.

It is difficult to evaluate the analytical results properly when the result pairs are very spread out. Therefore, the "true" value and the 20 % circle in Figure 13 is indicative only. The main

problem is the systematic deviations observed between the participating laboratories, indicating that the laboratories have applied different methods or slightly different modifications of a method, affecting the analytical results.

### Dissolved organic carbon

The results for this variable are presented in Figure 14, and the reported values are given in Table 5.14 (Appendix 4). Only 13 out of 36 laboratories determined this variable in the sample pair CD. A wet oxidation technique with UV and peroxodisulfate is used by six laboratories, and five laboratories used a combustion technique. There is no evidence for any differences in the reported results determined with these two methods for the samples used in this intercomparison. However, it is rather strange that the median value of the reported results determined by the UV/peroxodisulfate method is higher than the corresponding combustion results. Two laboratories used a photometric method based on phenolphthalein.

The great circle in Figure 14 and 15 is representing a general target accuracy of ± 20 %. Only two laboratories reported results located outside this limit.

### Chemical oxygen demand, COD-Mn

The results for this parameter are presented in Figure 15, and the reported values are given in Table 5.15 (Appendix 4). Only some few of the laboratories determined this parameter, which was included in the intercomparison because there are laboratories which do not have equipment for the determination of dissolved organic carbon. Random effects are dominating the two deviating result pairs in Figure 15.

## DISCUSSION

The general rule for target accuracies, outlined in the Manual for Chemical and Biological Monitoring (1), shall normally be used as acceptance limits for the results of the intercomparison test. These limits are corresponding to either the detection limit of the method, or 20 % of the true value, whichever being the greater.

In table 2 an evaluation of the results of this intercomparison is presented, based on the target accuracy. For pH the general target accuracy is ± 0.1 pH units, and less than 50 % of the result pairs are found within these accuracy limits. However, we have chosen to extend the acceptance limit to ± 0.2 pH units, because of the great spread of the results for these two samples which are weakly acid and neutral, respectively, and therefore are supposed not to be completely in $CO_2$-equilibrium.

In Table 2 is summarized an evaluation of the results of intercomparison 9610, where the number and percentage of acceptable results for the acceptance limits are given. 70 % of the results are acceptable when compared to the acceptance limits given above. For the reported results in this intercomparison, on average, about one laboratory out of four is located outside

the acceptance limit. By some improvement of the routine analytical method, these laboratories should obtain results with better comparablility to the others in this laboratory group.

**Table 2. Evaluation of the results of intercalibration 9509. N is the number of result pairs reported, and n is the number of acceptable results within the given target accuracy. Numbers in brackets are not evaluated.**

| Variable | Sample pair | N | Limit | n | % |
|---|---|---|---|---|---|
| pH | AB | 33 | 0.2* | 18 | 55 |
| Conductivity | AB | 32 | 20 % | 27 | 84 |
| Alkalinity | AB | ( 27 ) | 20 % | ( 5 ) | - |
| Nitrate + nitrite-nitrogen | AB | 33 | 20 % | 28 | 85 |
| Chloride | AB | 32 | 20 % | 14 | 44 |
| Sulfate | AB | 32 | 20 % | 24 | 75 |
| Calcium | AB | 32 | 20 % | 28 | 88 |
| Magnesium | AB | 32 | 20 % | 25 | 78 |
| Sodium | AB | 33 | 20 % | 27 | 82 |
| Potassium | AB | 33 | 20 % | 19 | 58 |
| Aluminium, total | AB | 17 | 20 % | 6 | 35 |
| Aluminium, reactive | CD | ( 9 ) | 20 % | ( 4 ) | - |
| Aluminium, non-labile | CD | ( 8 ) | 20 % | ( 1 ) | - |
| Dissolved organic carbon | CD | 13 | 20 % | 11 | 85 |
| Chemical oxygen demand | CD | 6 | 20 % | 4 | 67 |
| Sum | | 328 | | 231 | 70 |

* The accetance limit is extended from 0.1 to 0.2 pH units

For three variables: alkalinity, reactive and non-labile aluminium, we have decided not to evaluate the results reported by the participants, because of the very great spread of the reported values.

For pH the problem of comparability between the reported results is dominated by the fact that the pH values in nearly neutral solutions are much more spread out than in mor acid solutions, compare sample B, which is nearly neutral, to sample A which is weakly acid. For sample B the difference between pH values measured in a stirred solution is systematically lower than in a quiescent solution. This problem has been demonstrated through several intercomparisons, and will remain as a problem as long as different methods for pH determination are used at the participating laboratories.

For alkalinity, we also have observed earlier, that the reported results for solutions with low alkalinity values are spread out much more than in solutions with higher concentrations of bicarbonate. At this intecomparison we have a special problem in addition to the traditional

one, because of the lack of agreement between pH and alkalinity for sample A, caused by the high concentration of organic anions.

For chloride we also have observed at earlier intercomparisons a worse comparability than for other anions. This is probably due to interferences, and this is clearly demonstrated this time as the high concentration of acetate is affecting the comparability of the results for sample A, while the comparability of the chloride results in sample B is rather good. This is suggestive, because this situation demonstrates that the methods used for routine analysis of surface water is rather vulnerable if contaminated samples or " unnormal" samples are entered into the series of chloride analysis.

To evaluate the determination of aluminium fractions, it seems to be necessary that the laboratories normalize their analytical methods to improve the comparability for these variables. There is still some confusion about what aluminium fractions should be determined. The intention in this intercomparison was to compare the results for the variables printed in bold in the scheme presented in Figure 16. There have obviously been reported some results for other fractions than we asked for. This may be due to the fact that the Programme centre has chosen the definitions of aluminium species given by Driscoll (7), well aware of the possibility that other laboratories may use a slightly different definition system.

The non-exchangeable aluminium initially present in the samples of this intercomparison, is assumed to be associated with organic matter. The fact that the laboratories used different modifications and even different methods for the determination of aluminium species, may explain some of the great spread of these results.

**Figure 16. Schematic representation of aluminium fractions according to Driscoll (7).**

<table>
<tr><td rowspan="3">Aluminium measurement</td><td colspan="3">Total aluminium<br>acid digested</td></tr>
<tr><td colspan="2">Reactive aluminium<br>Total monomeric aluminium, no acid digestion</td><td></td></tr>
<tr><td>Monomeric aluminium, cation exchange treated</td><td></td><td></td></tr>
<tr><td>Aluminium fraction</td><td>Non-labile monomeric aluminium</td><td>Labile monomeric aluminium</td><td>Acid soluble aluminium</td></tr>
<tr><td>Fraction composition</td><td>Monomeric alumino-organic complexes</td><td>Free aluminium, monomeric aluminiumsulfate, fluoride and hydroxide complexes</td><td>Colloidal polymeric aluminium, strong alumino-organic complexes</td></tr>
</table>

## CONCLUSION

Rather poor comparability was observed for the results of pH, alkalinity, chloride and aluminium species. Obviously some laboratories had special problems for determining these variables in sample A, which contained rather high concentration of organic anions. Therefore it was decided not to evaluate the reported results for alkalinity and aluminium fractions.

For the other analytical variables 70 % of the reported results were lying within the general target accuracy of ± 20 %. The laboratories which reported results outside this limit should improve their methods to obtain a better comparability. Generally, the application of manual analytical methods seem to be less suited for the water samples which are analyzed in this programme, as the detection limit of many manual methods are too high. If these laboratories are going to analyze rather low concentration samples in the future, it is important that they lower the detectin limit of their methods.

To improve the comparability of the analytical results for aluminium fractions, it seems to be necessary to normalize the analytical methods and determination techniques used for these determinations, for instance to meet the definitions given in Figure 16.

A total error of ± 0.2 pH units seems to be a reasonable assessment of the accuracy for pH measurements when weakly acid or neutral water samples - which is not in $CO_2$ equilibrium - are analyzed.

Good results were reported for conductivity, nitrate + nitrite, calcium, sodium and dissolved organic carbon.

Only 36 laboratories submitted results for this intercomparison. Some laboratories have informed that the summer is a less suitable part of the year for participation in intercomparisons. We therefore will organize the next intercomparisons during the winter or spring time .

## LITERATURE


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## APPENDIX I. Participants of intercomparison 9610

| Identity | Laboratory | Country |
|---|---|---|
| 1 | USGS, WRD Co District | USA |
| 2 | Swiss Federal Institute for Forest, Snow and | Switzerland |
| 3 | Great Lakes Forest Centre | Canada |
| 4 | SWELAB | Sweden |
| 5 | ITMm Stockholm University | Sweden |
| 6 | Czech Geologic Survey Prague | Czech Republic |
| 7 | Water Pollution Observation Laboratory | Latvia |
| 8 | Research and Engin. Inst. for Environment | Romania |
| 10 | Environmental Research Unit | Ireland |
| 11 | Bayerische Landesamt fur Wasserwirtschaft | Germany |
| 12 | Estonian Environment Research Laboratory | Estonia |
| 13 | Polish Academy of Sciences | Poland |
| 14 | T.G.Masaryk Water Research Institute | Czech Republic |
| 15 | Karntner Institut fur Seewasser Forschung | Austria |
| 16 | IVL | Sweden |
| 17 | University of Barcelona | Spain |
| 19 | Swedish University for Agricultural Sciences | Sweden |
| 20 | Länsstyrelsen i Kalmar Län | Sweden |
| 21 | Landesumweltamt Nordrhein Westfalen | Germany |
| 22 | National Rivers Authority | United Kingdom |
| 24 | Kola Science Center | Russia |
| 26 | Lapland Water and Environment District | Finland |
| 27 | Staatliche Umweltbetriebgesellschaft im UBG | Germany |
| 28 | CNR Istituto Italiano di Idrobiologia | Italy |
| 29 | Uusima Regional Environmental Centre | Finland |
| 30 | South Estonian Environm. Protection Agency | Estonia |
| 31 | Kymen Water and Environment Dustrict | Finland |
| 32 | Institute of Environmental Protection | Poland |
| 33 | Institute of Hydrobiology | Czech Republic |
| 34 | Environmental Protection Ministry | Lithuania |
| 35 | National Board of Waters and the Environment | Finland |
| 36 | Institute for Ecology of Industrial Areas | Poland |
| 38 | DAFS Freshwater Laboratory | Scotland |
| 39 | University of Alberta | Canada |
| 40 | Centre National de la Recherche Scientifique | France |
| 41 | Ministry of Environment and Ecology | Canada |
| 42 | Norwegian Institute for Water Research | Norway |

## APPENDIX 2

### Preparation of samples

The sample solutions were prepared from natural water collected at two locations, Buvatn in the Langtjern area, Sørkedalselva outside Oslo, and from a marsh area outside Oslo (Hellerudmyra). Raw water was collected in polyethylene containers and brought to the laboratory for storage. For sample A was used the water from a lake called Buvatn, pH of this sample was lowered by the addition of acetic acid. Sample B was prepared from water from a creek called Sørkedalselva. Buvatn was also used for the sample C, and water from Hellerudmyra was mixed up with the creek water for sample D. These solutions were stored at room temperature for several weeks at the laboratory. During this stabilization period suspended matter settled. The solutions were filtrated through 0.45 µm membrane filter, and small aliquouts were removed from the filtrate to determine the concentrations of the parameters of interest.

A few days before mailing to the participants, the solutions were transferred to 1/2 liter (and some few 1 liter) polyethylene bottles with screw cap. These samples were stored at room temperature until mailing to the participating laboratories.

**Table 3. Summary of the control analyses.**

| Parameter | Sample A | | Sample B | | Sample C | | Sample D | |
|---|---|---|---|---|---|---|---|---|
| | Mean | Std. dev. | Mean | Std. dev. | Mean | Std. dev. | Mean | Std. dev. |
| pH | 5.07 | 0.02 | 7.06 | 0.06 | | | | |
| Conductivity mS/m | 12.8 | 0.15 | 3.85 | 0.10 | | | | |
| Alkalinity mmol/l | 20.7 | 0.8 | 11.2 | 0.8 | | | | |
| Nitrate/nitrite µg/l | 168 | 5.8 | 192 | 12.6 | | | | |
| Chloride mg/l | 0.67 | 0.23 | 1.47 | 0.06 | | | | |
| Sulfate mg/l | 2.33 | 0.31 | 3.69 | 0.12 | | | | |
| Calcium mg/l | 1.54 | 0.02 | 5.40 | 0.07 | | | | |
| Magnesium mg/l | 0.187 | 0.006 | 0.443 | 0.006 | | | | |
| Sodium mg/l | 0.827 | 0.032 | 1.217 | 0.006 | | | | |
| Potassium mg/l | 0.203 | 0.006 | 0.300 | 0 | | | | |
| Aluminium total, µg/l | | | | | 82 | 9.2 | 115 | 1.5 |
| Reactive aluminium µg/l | | | | | 55 | 1.2 | 103 | 4.2 |
| Non-labile alumin. µg/l | | | | | 47 | 2.1 | 31 | 2.6 |
| Diss.org. C mg/l | | | | | 3.77 | 0.15 | 3.30 | 0.17 |
| COD.Mn, mg/l | | | | | 3.94 | 0.23 | 3.29 | 0.19 |

### Sample control analyses

During the intercalibration period, three sets of samples were randomly selected from the batch for control analyses. The determinations were carried out by the laboratory at the Programme Centre, the first sample set being analyzed some days before mailing of the samples to the participants. The last sample was analyzed at the middle of July 1995. A summary of the control results is presented in Table 3. The control results confirmed that the stability of the sample solutions were acceptable during the intercalibration period.

## APPENDIX 3

### Treatment of analytical data

The intercalibration was carried out by the method of Youden. This procedure requires two samples to be analyzed, and every laboratory shall report only one result for each sample and parameter. In a coordinate system the result of sample 2 is plotted against the result of sample 1 (see Figures 1 - 15).

The graphical presentation creates a possibility to distinguish between random and systematic errors affecting the results. The two stright lines drawn in the diagram are representing the true values of the samples; or - as in this case, when the true value is not known - the median value of the results from all the participating laboratories. The diagram is thus divided into four quadrants. In a hypothetical case, when the analysis is affected by random errors only, the results will spread randomly over the four quadrants.

However, the results are usually located in the lower left and the upper right quadrant, constituting a characteristic elliptical pattern along the 45 ° line. This is reflecting the fact that many laboratories - due to systematic deviations - have attained too low or too high values for both samples.

The acceptance limit of the results may be represented by a circle with its centrum at the intersection of the two straight lines in the diagram (true or median values). The distance between the centrum of the circle, and the mark representing the laboratory, is a measure of the total error of the results. The distance along the 45 ° line is giving the mangitude of the systematic error, while the distance perpendicular to the 45 ° line is indicating the magnitude of the random error. The location of the laboratory in the diagram is an important information about the size and type of analytical error, making it easier to disclose the cause of error.

The statistical treatment of the analytical results was accomplished in this way: Pairs of results where one or both of the values are lying outside the true value ± 50 %, are omitted from the statistical calculations. The remaining results are used for the calculation of the mean value (x) and the standard deviation (s). Now the pairs of results where both of the values are lying outside $x \pm 3s$, are omitted. The remaining results are used for a final calculation, the results of which are presented in the tables 5.1 - 5.15. Results being omitted from the calculations, are marked with the letter "U".

**APPENDIX 4** **Table 4. The results reported by the participants**

| Identity | pH A | pH B | Cond A | Cond B | Alk A | Alk B | NO3+NO2 A | NO3+NO2 B |
|---|---|---|---|---|---|---|---|---|
| 1 | 5.03 | 7.46 | 13.1 | 3.99 | 20.4 | 10.7 | 167 | 179 |
| 2 | | | | | | | | |
| 3 | 4.95 | 7 | 12.63 | 3.96 | -22.66 | 10.42 | 153 | 174 |
| 4 | | | | | | | | |
| 5 | 5.02 | 7.05 | 13.1 | 4 | < 0.1 | 12.505 | 175 | 200 |
| 6 | 5.06 | 7.08 | 13.1 | 3.98 | 40.74 | 10.31 | 181 | 194 |
| 7 | 5.16 | 7.33 | 12.8 | 3.84 | < 1.5 | 9 | 190 | 178 |
| 8 | 5.4 | 6.86 | | | 53 | 19.8 | 2490 | 3058 |
| 10 | 4.94 | 6.74 | 14 | 5.4 | 32 | 14.5 | 156 | 181 |
| 11 | 4.76 | 6.8 | 13.29 | 4.09 | | 13.9 | 161 | 187 |
| 12 | 5.1 | 7.2 | 12.5 | 3.8 | 9.5 | 10 | 130 | 190 |
| 13 | 4.54 | 6.34 | 16.42 | 5.68 | | | 159 | 176 |
| 14 | 4.75 | 6.72 | 10.9 | 3.4 | 36.5 | 13 | 180 | 226 |
| 15 | 4.9 | 6.65 | 13.2 | 4.2 | | | 176 | 187 |
| 16 | 5.04 | 7.23 | 12.64 | 3.79 | | | 160 | 191 |
| 19 | 5.05 | 7.12 | 13.8 | 4.24 | -26.2 | 9.8 | 153 | 178 |
| 20 | 5.04 | 7.1 | 13.2 | 4.05 | < 0.5 | 12.8 | | |
| 21 | 5.07 | 7.13 | 13.34 | 4.08 | | | 160 | 170 |
| 22 | 4.94 | 6.93 | 12.4 | 3.9 | 7.03 | 10.67 | 159 | 202 |
| 24 | 5.04 | 6.98 | 11.3 | 3.8 | < 0.5 | 10 | 148 | 154 |
| 26 | 5 | 7.2 | 12.9 | 4 | 10.6 | 12.8 | 150 | 180 |
| 27 | 4.8 | 6.9 | 11 | 1.8 | 69 | 30 | < 600 | < 600 |
| 28 | 5.04 | 7.15 | 12.59 | 3.85 | 0 | 10.9 | 162 | 187 |
| 29 | | | | | | | 157 | 188 |
| 30 | 4.75 | 6.55 | 13.2 | 4.03 | 26 | 11.5 | 260 | 150 |
| 31 | 4.9 | 7.07 | 13.2 | 4.05 | 12.5 | 10.5 | 161 | 186 |
| 32 | 4.89 | 7.05 | 14 | 4.2 | | | 171 | 181 |
| 33 | 5.01 | 7.13 | 13.1 | 4.01 | 22 | 11 | 155 | 170 |
| 34 | 5.05 | 7.2 | 13.2 | 3.9 | 1.22 | 12.81 | 150 | 188 |
| 35 | 5.08 | 6.66 | 13.03 | 4 | | | 167 | 197.6 |
| 36 | 4.81 | 6.82 | 11.28 | 3.36 | < 0.02 | 11.36 | 160 | 190 |
| 38 | 5.08 | 6.88 | 12.3 | 3.6 | 13.2 | 10.4 | 160 | 196 |
| 39 | 4.9 | 6.78 | 13.1 | 4 | 21.13 | 12.13 | 137.8 | 155.3 |
| 40 | 5.06 | 6.95 | 13 | 4 | 44.55 | 10.7 | 154 | 168 |
| 41 | 4.97 | 7.29 | 13.4 | 3.8 | 20.6 | 12.2 | 185 | 165 |
| 42 | 5.08 | 7.08 | 13 | 3.93 | 20.2 | 10.7 | 165 | 190 |

| Identity | Cl A | Cl B | SO4 A | SO4 B | Ca A | Ca B | Mg A | Mg B |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.58 | 1.43 | 3.14 | 4.23 | 1.54 | 5.49 | 0.2 | 0.46 |
| 2 | | | | | 1.8 | 6.82 | 0.25 | 0.56 |
| 3 | 0.339 | 1.371 | 2.53 | 3.46 | 1.593 | 5.399 | 0.183 | 0.431 |
| 4 | | | | | | | | |
| 5 | 7.63 | 1.31 | 3.02 | 3.65 | 1.503 | 5.429 | 0.195 | 0.438 |
| 6 | 0.74 | 1.49 | 3.09 | 3.6 | 1.48 | 5.1 | 0.18 | 0.39 |
| 7 | 1.42 | 1.77 | 3.22 | 2.35 | 1.08 | 5.1 | 0.2 | 0.49 |
| 8 | 12.78 | 17.75 | 2.62 | 0.39 | 2 | 5.41 | 1.82 | 1.82 |
| 10 | 0.72 | 1.34 | 2.68 | 3.67 | 1.43 | 5.28 | 0.18 | 0.44 |
| 11 | 0.65 | 1.45 | 2.78 | 3.67 | 1.53 | 5.29 | 0.2 | 0.45 |
| 12 | 3.93 | 1.38 | 2.7 | 3.6 | 0.93 | 4.27 | 0.2 | 0.41 |
| 13 | 0.753 | 1.366 | 2.565 | 3.27 | 1.42 | 5.82 | 0.19 | 0.36 |
| 14 | 0.48 | 1.35 | 1.42 | 2.03 | | | | |
| 15 | 0.7 | 1.5 | 2.7 | 3.5 | 1.4 | 4.7 | 0.2 | 0.4 |
| 16 | 0.91 | 1.54 | 2.96 | 3.85 | 1.49 | 4.85 | 0.2 | 0.44 |
| 19 | 8.26 | 1.49 | 2.78 | 3.55 | 1.61 | 5.29 | 0.19 | 0.44 |
| 20 | | | | | | | | |
| 21 | < 1 | 1.4 | 2.7 | 3.5 | 1.59 | 5.58 | 0.2 | 0.474 |
| 22 | 0.9 | 1.7 | 2.82 | 3.76 | 1.37 | 5.48 | 0.2 | 0.46 |
| 24 | 0.72 | 1.53 | 2.54 | 3.43 | 1.33 | 4.85 | 0.17 | 0.42 |
| 26 | 0.43 | 1.3 | 2.7 | 3.6 | 1.5 | 5.3 | 0.2 | 0.4 |
| 27 | < 5 | < 5 | 3.6 | 4.3 | 2.1 | 5.3 | 0.36 | 0.54 |
| 28 | 0.66 | 1.52 | 2.84 | 3.78 | 1.01 | 5.18 | 0.23 | 0.44 |
| 29 | 0.38 | 1.37 | 2.71 | 3.67 | 1.54 | 5.39 | 0.2 | 0.45 |
| 30 | 8 | 1.2 | 3.4 | 3.9 | 2.45 | 4.8 | 0.49 | 0.97 |
| 31 | | | | | | | | |
| 32 | 0.731 | 1.44 | 3.02 | 3.69 | 1.539 | 5.42 | 0.191 | 0.443 |
| 33 | 0.7 | 1.44 | 3.02 | 4.06 | 1.68 | 5.39 | 0.18 | 0.45 |
| 34 | 1.17 | 1.8 | 2.2 | 3.6 | 1.62 | 4.45 | 0.37 | 1.83 |
| 35 | 0.66 | 1.48 | 2.76 | 3.75 | 1.59 | 5.3 | 0.19 | 0.45 |
| 36 | 1.73 | 1.5 | 2.47 | 3.41 | 1.42 | 4.9 | 0.16 | 0.38 |
| 38 | 0.5 | 1.33 | 2.7 | 3.67 | 1.31 | 5.88 | 0.21 | 0.46 |
| 39 | 1.2 | 2.9 | 1.5 | 3.9 | 1.48 | 5.31 | 0.2 | 0.45 |
| 40 | 0.532 | 1.453 | 2.88 | 3.94 | 1.52 | 5.33 | 0.19 | 0.44 |
| 41 | 0.78 | 1.52 | 2.8 | 3.75 | 1.4 | 4.8 | 0.196 | 0.438 |
| 42 | 0.8 | 1.5 | 2.4 | 3.57 | 1.55 | 5.36 | 0.19 | 0.45 |

| Identity | Na A | Na B | K A | K B | Al C | Al D | Al-R C | Al-R D |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.89 | 1.31 | 0.03 | 0.47 | | | | |
| 2 | 0.92 | 1.31 | < 0.45 | < 0.45 | | | | |
| 3 | 0.899 | 1.315 | 0.225 | 0.338 | 60.8 | 115.1 | | |
| 4 | | | | | 82 | 110 | 23 | 93 |
| 5 | 0.943 | 1.264 | 0.234 | 0.313 | 81.9 | 103.8 | 26.5 | 109.9 |
| 6 | 0.8 | 1.15 | 0.22 | 0.32 | | | | |
| 7 | 1.01 | 1.31 | 0.22 | 0.3 | | | | |
| 8 | 0.779 | 1.147 | 0.197 | 0.27 | 49.37 | 59.44 | 46.17 | 50.09 |
| 10 | 0.88 | 1.26 | 0.21 | 0.33 | | | | |
| 11 | 1.14 | 1.49 | 0.25 | 0.38 | | | | |
| 12 | 1.1 | 1.6 | 0.2 | 0.3 | | | | |
| 13 | 1.12 | 1.5 | 0.27 | 0.25 | | | | |
| 14 | 0.885 | 1.23 | 0.22 | 0.31 | 115 | 133 | | |
| 15 | 1 | 1.3 | 0.3 | 0.4 | 122.3 | 145.3 | | |
| 16 | 0.8 | 1.2 | 0.238 | 0.35 | 95.3 | 118 | | |
| 19 | 0.91 | 1.28 | 0.23 | 0.31 | | | | |
| 20 | | | | | | | 90 | 115 |
| 21 | 0.806 | 1.23 | < 0.5 | < 0.5 | | | | |
| 22 | 0.88 | 1.26 | 0.22 | 0.35 | 90 | 115 | 80 | 150 |
| 24 | 0.83 | 1.3 | 0.22 | 0.32 | 78 | 114 | 25 | 90 |
| 26 | 0.9 | 1.3 | 0.2 | 0.3 | | | | |
| 27 | 1.2 | 1.3 | 1.2 | 1.1 | | | | |
| 28 | 0.88 | 1.29 | 0.14 | 0.3 | | | | |
| 29 | 0.89 | 1.31 | 0.24 | 0.35 | | | | |
| 30 | 1.5 | 1.5 | 0.4 | 0.4 | | | | |
| 31 | | | | | | | | |
| 32 | 0.903 | 1.307 | 0.229 | 0.342 | 84.5 | 116.2 | | |
| 33 | 0.89 | 1.28 | 0.34 | 0.29 | 65 | 92 | | |
| 34 | 0.98 | 1.28 | 0.18 | 0.27 | | | | |
| 35 | 0.81 | 1.2 | 0.23 | 0.32 | 83.8 | 116 | 19.9 | 105.4 |
| 36 | 1.13 | 1.62 | 0.18 | 0.38 | 67.4 | 103.1 | | |
| 38 | 0.87 | 1.3 | 0.29 | 0.2 | 47 | 93 | 11 | 77 |
| 39 | 0.86 | 1.25 | 0.23 | 0.35 | | | | |
| 40 | 0.9 | 1.24 | 0.23 | 0.35 | 86 | 111 | | |
| 41 | 0.916 | 1.31 | 0.222 | 0.338 | 104 | 133 | | |
| 42 | 0.84 | 1.22 | 0.2 | 0.3 | 77 | 114 | 54 | 100 |

| Identity | Al-II C | Al-II D | DOC C | DOC D | COD-Mn C | COD-Mn D |
|---|---|---|---|---|---|---|
| 1 | | | | | | |
| 2 | | | | | | |
| 3 | | | 3.526 | 3.04 | | |
| 4 | 57 | 17 | | | 4 | 3 |
| 5 | 21.8 | 23 | 4.22 | 3.49 | | |
| 6 | | | | | | |
| 7 | | | | | | |
| 8 | | | | | 1.58 | 0.63 |
| 10 | | | | | | |
| 11 | | | | | | |
| 12 | | | | | | |
| 13 | | | | | | |
| 14 | | | | | 3.96 | 3.22 |
| 15 | | | 3.7 | 3.2 | | |
| 16 | | | 3.66 | 3.17 | | |
| 19 | | | 3.6 | 3.3 | 4.08 | 3.3 |
| 20 | 80 | 40 | | | | |
| 21 | | | | | | |
| 22 | 54 | 43 | 4.4 | 3.9 | | |
| 24 | 53 | 24 | 4.03 | 3.18 | | |
| 26 | | | | | | |
| 27 | | | | | | |
| 28 | | | | | | |
| 29 | | | | | | |
| 30 | | | | | | |
| 31 | | | | | | |
| 32 | | | | | | |
| 33 | | | 5.2 | 4.2 | | |
| 34 | | | | | | |
| 35 | 7.9 | 11.5 | 3.72 | 3.38 | | |
| 36 | | | | | 5.8 | 3 |
| 38 | 36 | 16 | 3.8 | 3.25 | | |
| 39 | | | | | | |
| 40 | | | 3.45 | 3.03 | | |
| 41 | | | 3.5 | 3.2 | | |
| 42 | 46 | 28 | 3.8 | 3.4 | 3.8 | 3.5 |

## Table 5. 1 . Statistics - pH

All methods
Unit:

Sample A

| | | | |
|---|---|---|---|
| Number of participants | 33 | Range | 0.86 |
| Number of omitted results | 0 | Variance | 0.02 |
| True value | 5.02 | Standard deviation | 0.15 |
| Mean value | 4.98 | Relative Standard deviation | 3.00 % |
| Median value | 5.02 | Relative error | -0.90 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 13 | 4.54 | 22 | 4.94 | 34 | 5.05 |
| 14 | 4.75 | 3 | 4.95 | 19 | 5.05 |
| 30 | 4.75 | 41 | 4.97 | 40 | 5.06 |
| 11 | 4.76 | 26 | 5.00 | 6 | 5.06 |
| 27 | 4.80 | 33 | 5.01 | 21 | 5.07 |
| 36 | 4.81 | 5 | 5.02 | 35 | 5.08 |
| 32 | 4.89 | 1 | 5.03 | 42 | 5.08 |
| 39 | 4.90 | 24 | 5.04 | 38 | 5.08 |
| 15 | 4.90 | 28 | 5.04 | 12 | 5.10 |
| 31 | 4.90 | 16 | 5.04 | 7 | 5.16 |
| 10 | 4.94 | 20 | 5.04 | 8 | 5.40 |

Sample B

| | | | |
|---|---|---|---|
| Number of participants | 33 | Range | 1.12 |
| Number of omitted results | 0 | Variance | 0.06 |
| True value | 7.05 | Standard deviation | 0.24 |
| Mean value | 6.98 | Relative Standard deviation | 3.40 % |
| Median value | 7.05 | Relative error | -1.00 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 13 | 6.34 | 27 | 6.90 | 19 | 7.12 |
| 30 | 6.55 | 22 | 6.93 | 33 | 7.13 |
| 15 | 6.65 | 40 | 6.95 | 21 | 7.13 |
| 35 | 6.66 | 24 | 6.98 | 28 | 7.15 |
| 14 | 6.72 | 3 | 7.00 | 12 | 7.20 |
| 10 | 6.74 | 32 | 7.05 | 34 | 7.20 |
| 39 | 6.78 | 5 | 7.05 | 26 | 7.20 |
| 11 | 6.80 | 31 | 7.07 | 16 | 7.23 |
| 36 | 6.82 | 42 | 7.08 | 41 | 7.29 |
| 8 | 6.86 | 6 | 7.08 | 7 | 7.33 |
| 38 | 6.88 | 20 | 7.10 | 1 | 7.46 |

U = Omitted results

## Table 5. 2 . Statistics - Conductivity

All methods
Unit: mS/m

Sample A

| | | | |
|---|---|---|---|
| Number of participants | 32 | Range | 3.1 |
| Number of omitted results | 3 | Variance | 0.48 |
| True value | 13.1 | Standard deviation | 0.69 |
| Mean value | 12.85 | Relative Standard deviation | 5.30 % |
| Median value | 13.1 | Relative error | -1.90 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 14 | 10.90 | 26 | 12.90 | 31 | 13.20 |
| 27 | 11.00 U | 40 | 13.00 | 34 | 13.20 |
| 36 | 11.28 | 42 | 13.00 | 30 | 13.20 |
| 24 | 11.30 | 35 | 13.03 | 11 | 13.29 |
| 38 | 12.30 | 33 | 13.10 | 21 | 13.34 |
| 22 | 12.40 | 1 | 13.10 | 41 | 13.40 |
| 12 | 12.50 | 39 | 13.10 | 19 | 13.80 |
| 28 | 12.59 | 6 | 13.10 | 10 | 14.00 U |
| 3 | 12.63 | 5 | 13.10 | 32 | 14.00 |
| 16 | 12.64 | 20 | 13.20 | 13 | 16.42 U |
| 7 | 12.80 | 15 | 13.20 | | |

Sample B

| | | | |
|---|---|---|---|
| Number of participants | 32 | Range | 0.88 |
| Number of omitted results | 3 | Variance | 0.04 |
| True value | 4 | Standard deviation | 0.2 |
| Mean value | 3.93 | Relative Standard deviation | 5.10 % |
| Median value | 3.99 | Relative error | -1.90 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 27 | 1.80 U | 22 | 3.90 | 30 | 4.03 |
| 36 | 3.36 | 42 | 3.93 | 20 | 4.05 |
| 14 | 3.40 | 3 | 3.96 | 31 | 4.05 |
| 38 | 3.60 | 6 | 3.98 | 21 | 4.08 |
| 16 | 3.79 | 1 | 3.99 | 11 | 4.09 |
| 24 | 3.80 | 39 | 4.00 | 15 | 4.20 |
| 12 | 3.80 | 35 | 4.00 | 32 | 4.20 |
| 41 | 3.80 | 40 | 4.00 | 19 | 4.24 |
| 7 | 3.84 | 26 | 4.00 | 10 | 5.40 U |
| 28 | 3.85 | 5 | 4.00 | 13 | 5.68 U |
| 34 | 3.90 | 33 | 4.01 | | |

U = Omitted results

## Table 5. 3 . Statistics - Alkalinity

All methods
Unit: mg/l

Sample A

| | | | |
|---|---|---|---|
| Number of participants | 27 | Range | 15.4 |
| Number of omitted results | 18 | Variance | 26.6 |
| True value | 20.4 | Standard deviation | 5.16 |
| Mean value | 18.51 | Relative Standard deviation | 25.30 % |
| Median value | 20.4 | Relative error | -9.20 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 11 | U | 34 | 1.22 U | 39 | 21.13 |
| 7 | < 1.5 U | 22 | 7.03 U | 33 | 22 |
| 20 | < 0.5 U | 12 | 9.5 U | 30 | 26 |
| 24 | < 0.5 U | 26 | 10.6 | 10 | 32 U |
| 36 | < 0.02 U | 31 | 12.5 | 14 | 36.5 U |
| 5 | < 0.1 U | 38 | 13.2 | 6 | 40.74 U |
| 19 | -26.2 U | 42 | 20.2 | 40 | 44.55 U |
| 3 | -22.66 U | 1 | 20.4 | 8 | 53 U |
| 28 | 0 U | 41 | 20.6 | 27 | 69 U |

Sample B

| | | | |
|---|---|---|---|
| Number of participants | 27 | Range | 2.4 |
| Number of omitted results | 18 | Variance | 0.76 |
| True value | 11 | Standard deviation | 0.87 |
| Mean value | 11.33 | Relative Standard deviation | 7.90 % |
| Median value | 11 | Relative error | 3.00 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 7 | 9.0 U | 1 | 10.7 | 5 | 12.51 U |
| 19 | 9.8 U | 40 | 10.7 U | 20 | 12.8 U |
| 24 | 10.0 U | 42 | 10.7 | 26 | 12.8 |
| 12 | 10.0 U | 28 | 10.9 U | 34 | 12.81 U |
| 6 | 10.31 U | 33 | 11.0 | 14 | 13.0 U |
| 38 | 10.4 | 36 | 11.36 U | 11 | 13.9 U |
| 3 | 10.42 U | 30 | 11.5 | 10 | 14.5 U |
| 31 | 10.5 | 39 | 12.13 | 8 | 19.8 U |
| 22 | 10.67 U | 41 | 12.2 | 27 | 30 U |

U = Omitted results

## Table 5. 4 . Statistics - Nitrate + nitrite-nitrogen

All methods
Unit: Ág/l

Sample A

| | | | |
|---|---|---|---|
| Number of participants | 33 | Range | 60 |
| Number of omitted results | 3 | Variance | 171 |
| True value | 160 | Standard deviation | 13 |
| Mean value | 161 | Relative Standard deviation | 8.20 % |
| Median value | 160 | Relative error | 0.90 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 27 | < 600 U | 29 | 157 | 1 | 167 |
| 12 | 130 | 13 | 159 | 35 | 167 |
| 39 | 138 | 22 | 159 | 32 | 171 |
| 24 | 148 | 21 | 160 | 5 | 175 |
| 34 | 150 | 16 | 160 | 15 | 176 |
| 26 | 150 | 36 | 160 | 14 | 180 |
| 3 | 153 | 38 | 160 | 6 | 181 |
| 19 | 153 | 31 | 161 | 41 | 185 |
| 40 | 154 | 11 | 161 | 7 | 190 |
| 33 | 155 | 28 | 162 | 30 | 260 U |
| 10 | 156 | 42 | 165 | 8 | 2490 U |

Sample B

| | | | |
|---|---|---|---|
| Number of participants | 33 | Range | 72 |
| Number of omitted results | 3 | Variance | 207 |
| True value | 187 | Standard deviation | 14 |
| Mean value | 184 | Relative Standard deviation | 7.70 % |
| Median value | 187 | Relative error | -1.80 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 27 | < 600 U | 19 | 178 | 12 | 190 |
| 30 | 150 U | 1 | 179 | 36 | 190 |
| 24 | 154 | 26 | 180 | 42 | 190 |
| 39 | 155 | 10 | 181 | 16 | 191 |
| 41 | 165 | 32 | 181 | 6 | 194 |
| 40 | 168 | 31 | 186 | 38 | 196 |
| 33 | 170 | 28 | 187 | 35 | 198 |
| 21 | 170 | 15 | 187 | 5 | 200 |
| 3 | 174 | 11 | 187 | 22 | 202 |
| 13 | 176 | 34 | 188 | 14 | 226 |
| 7 | 178 | 29 | 188 | 8 | 3058 U |

U = Omitted results

## Table 5. 5 . Statistics - Chloride

All methods
Unit: mg/l

Sample A

| | | | |
|---|---|---|---|
| Number of participants | 32 | Range | 0.53 |
| Number of omitted results | 12 | Variance | 0.02 |
| True value | 0.7 | Standard deviation | 0.14 |
| Mean value | 0.67 | Relative Standard deviation | 20.60 % |
| Median value | 0.7 | Relative error | -4.80 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 27 | < 5 U | 28 | 0.66 | 16 | 0.91 |
| 21 | < 1 U | 33 | 0.70 | 34 | 1.17 U |
| 3 | 0.34 U | 15 | 0.70 | 39 | 1.20 U |
| 29 | 0.38 | 24 | 0.72 | 7 | 1.42 U |
| 26 | 0.43 | 10 | 0.72 | 36 | 1.73 U |
| 14 | 0.48 | 32 | 0.73 | 12 | 3.93 U |
| 38 | 0.50 | 6 | 0.74 | 5 | 7.63 U |
| 40 | 0.53 | 13 | 0.75 | 30 | 8.00 U |
| 1 | 0.58 | 41 | 0.78 | 19 | 8.26 U |
| 11 | 0.65 | 42 | 0.80 | 8 | 12.78 U |
| 35 | 0.66 | 22 | 0.90 | | |

Sample B

| | | | |
|---|---|---|---|
| Number of participants | 32 | Range | 0.4 |
| Number of omitted results | 12 | Variance | 0.01 |
| True value | 1.45 | Standard deviation | 0.09 |
| Mean value | 1.45 | Relative Standard deviation | 6.50 % |
| Median value | 1.45 | Relative error | 0.20 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 27 | < 5 U | 21 | 1.40 U | 42 | 1.50 |
| 30 | 1.20 U | 1 | 1.43 | 41 | 1.52 |
| 26 | 1.30 | 33 | 1.44 | 28 | 1.52 |
| 5 | 1.31 U | 32 | 1.44 | 24 | 1.53 |
| 38 | 1.33 | 11 | 1.45 | 16 | 1.54 |
| 10 | 1.34 | 40 | 1.45 | 22 | 1.70 |
| 14 | 1.35 | 35 | 1.48 | 7 | 1.77 U |
| 13 | 1.37 | 6 | 1.49 | 34 | 1.80 U |
| 29 | 1.37 | 19 | 1.49 U | 39 | 2.90 U |
| 3 | 1.37 U | 36 | 1.50 U | 8 | 17.75 U |
| 12 | 1.38 U | 15 | 1.50 | | |

U = Omitted results

## Table 5. 6 . Statistics - Sulfate

All methods
Unit: mg/l

Sample A

| | | | |
|---|---|---|---|
| Number of participants | 32 | Range | 2.1 |
| Number of omitted results | 2 | Variance | 0.14 |
| True value | 2.77 | Standard deviation | 0.38 |
| Mean value | 2.77 | Relative Standard deviation | 13.60 % |
| Median value | 2.77 | Relative error | 0.20 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 14 | 1.42 U | 12 | 2.70 | 40 | 2.88 |
| 39 | 1.50 | 15 | 2.70 | 16 | 2.96 |
| 34 | 2.20 | 38 | 2.70 | 33 | 3.02 |
| 42 | 2.40 | 26 | 2.70 | 32 | 3.02 |
| 36 | 2.47 | 29 | 2.71 | 5 | 3.02 |
| 3 | 2.53 | 35 | 2.76 | 6 | 3.09 |
| 24 | 2.54 | 11 | 2.78 | 1 | 3.14 |
| 13 | 2.57 | 19 | 2.78 | 7 | 3.22 |
| 8 | 2.62 U | 41 | 2.80 | 30 | 3.40 |
| 10 | 2.68 | 22 | 2.82 | 27 | 3.60 |
| 21 | 2.70 | 28 | 2.84 | | |

Sample B

| | | | |
|---|---|---|---|
| Number of participants | 32 | Range | 1.95 |
| Number of omitted results | 2 | Variance | 0.11 |
| True value | 3.67 | Standard deviation | 0.34 |
| Mean value | 3.66 | Relative Standard deviation | 9.20 % |
| Median value | 3.67 | Relative error | -0.40 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 8 | 0.39 U | 12 | 3.60 | 35 | 3.75 |
| 14 | 2.03 U | 34 | 3.60 | 22 | 3.76 |
| 7 | 2.35 | 6 | 3.60 | 28 | 3.78 |
| 13 | 3.27 | 26 | 3.60 | 16 | 3.85 |
| 36 | 3.41 | 5 | 3.65 | 39 | 3.90 |
| 24 | 3.43 | 10 | 3.67 | 30 | 3.90 |
| 3 | 3.46 | 11 | 3.67 | 40 | 3.94 |
| 21 | 3.50 | 38 | 3.67 | 33 | 4.06 |
| 15 | 3.50 | 29 | 3.67 | 1 | 4.23 |
| 19 | 3.55 | 32 | 3.69 | 27 | 4.30 |
| 42 | 3.57 | 41 | 3.75 | | |

U = Omitted results

## Table 5. 7 . Statistics - Calcium

All methods
Unit: mg/l

Sample A

| | | | |
|---|---|---|---|
| Number of participants | 32 | Range | 1.17 |
| Number of omitted results | 2 | Variance | 0.05 |
| True value | 1.5 | Standard deviation | 0.23 |
| Mean value | 1.49 | Relative Standard deviation | 15.50 % |
| Median value | 1.5 | Relative error | -1.00 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 12 | 0.93 | 39 | 1.48 | 21 | 1.59 |
| 28 | 1.01 | 6 | 1.48 | 35 | 1.59 |
| 7 | 1.08 | 16 | 1.49 | 3 | 1.59 |
| 38 | 1.31 | 26 | 1.50 | 19 | 1.61 |
| 24 | 1.33 | 5 | 1.50 | 34 | 1.62 |
| 22 | 1.37 | 40 | 1.52 | 33 | 1.68 |
| 41 | 1.40 | 11 | 1.53 | 2 | 1.80 U |
| 15 | 1.40 | 32 | 1.54 | 8 | 2.00 |
| 36 | 1.42 | 1 | 1.54 | 27 | 2.10 |
| 13 | 1.42 | 29 | 1.54 | 30 | 2.45 U |
| 10 | 1.43 | 42 | 1.55 | | |

Sample B

| | | | |
|---|---|---|---|
| Number of participants | 32 | Range | 1.61 |
| Number of omitted results | 2 | Variance | 0.13 |
| True value | 5.3 | Standard deviation | 0.36 |
| Mean value | 5.22 | Relative Standard deviation | 6.70 % |
| Median value | 5.3 | Relative error | -1.50 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 12 | 4.27 | 10 | 5.28 | 3 | 5.40 |
| 34 | 4.45 | 11 | 5.29 | 8 | 5.41 |
| 15 | 4.70 | 19 | 5.29 | 32 | 5.42 |
| 41 | 4.80 | 27 | 5.30 | 5 | 5.43 |
| 30 | 4.80 U | 35 | 5.30 | 22 | 5.48 |
| 24 | 4.85 | 26 | 5.30 | 1 | 5.49 |
| 16 | 4.85 | 39 | 5.31 | 21 | 5.58 |
| 36 | 4.90 | 40 | 5.33 | 13 | 5.82 |
| 7 | 5.10 | 42 | 5.36 | 38 | 5.88 |
| 6 | 5.10 | 33 | 5.39 | 2 | 6.82 U |
| 28 | 5.18 | 29 | 5.39 | | |

U = Omitted results

## Table 5. 8 . Statistics - Magnesium

All methods
Unit: mg/l

Sample A

| | | | |
|---|---|---|---|
| Number of participants | 32 | Range | 0.07 |
| Number of omitted results | 5 | Variance | 0 |
| True value | 0.2 | Standard deviation | 0.01 |
| Mean value | 0.19 | Relative Standard deviation | 6.60 % |
| Median value | 0.2 | Relative error | -3.20 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 36 | 0.16 | 32 | 0.19 | 11 | 0.20 |
| 24 | 0.17 | 5 | 0.20 | 26 | 0.20 |
| 33 | 0.18 | 41 | 0.20 | 29 | 0.20 |
| 10 | 0.18 | 1 | 0.20 | 38 | 0.21 |
| 6 | 0.18 | 39 | 0.20 | 28 | 0.23 |
| 3 | 0.18 | 21 | 0.20 | 2 | 0.25 U |
| 35 | 0.19 | 12 | 0.20 | 27 | 0.36 U |
| 40 | 0.19 | 16 | 0.20 | 34 | 0.37 U |
| 13 | 0.19 | 15 | 0.20 | 30 | 0.49 U |
| 42 | 0.19 | 7 | 0.20 | 8 | 1.82 U |
| 19 | 0.19 | 22 | 0.20 | | |

Sample B

| | | | |
|---|---|---|---|
| Number of participants | 32 | Range | 0.13 |
| Number of omitted results | 5 | Variance | 0 |
| True value | 0.44 | Standard deviation | 0.03 |
| Mean value | 0.44 | Relative Standard deviation | 6.60 % |
| Median value | 0.44 | Relative error | -1.10 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 13 | 0.36 | 10 | 0.44 | 1 | 0.46 |
| 36 | 0.38 | 28 | 0.44 | 22 | 0.46 |
| 6 | 0.39 | 16 | 0.44 | 38 | 0.46 |
| 15 | 0.40 | 19 | 0.44 | 21 | 0.47 |
| 26 | 0.40 | 32 | 0.44 | 7 | 0.49 |
| 12 | 0.41 | 33 | 0.45 | 27 | 0.54 U |
| 24 | 0.42 | 39 | 0.45 | 2 | 0.56 U |
| 3 | 0.43 | 35 | 0.45 | 30 | 0.97 U |
| 41 | 0.44 | 11 | 0.45 | 8 | 1.82 U |
| 5 | 0.44 | 42 | 0.45 | 34 | 1.83 U |
| 40 | 0.44 | 29 | 0.45 | | |

U = Omitted results

## Table 5. 9 . Statistics - Sodium

All methods
Unit: mg/l

Sample A

| | | | |
|---|---|---|---|
| Number of participants | 33 | Range | 0.42 |
| Number of omitted results | 1 | Variance | 0.01 |
| True value | 0.89 | Standard deviation | 0.11 |
| Mean value | 0.92 | Relative Standard deviation | 12.20 % |
| Median value | 0.89 | Relative error | 3.80 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 8 | 0.78 | 22 | 0.88 | 2 | 0.92 |
| 16 | 0.80 | 14 | 0.89 | 5 | 0.94 |
| 6 | 0.80 | 33 | 0.89 | 34 | 0.98 |
| 21 | 0.81 | 1 | 0.89 | 15 | 1.00 |
| 35 | 0.81 | 29 | 0.89 | 7 | 1.01 |
| 24 | 0.83 | 3 | 0.90 | 12 | 1.10 |
| 42 | 0.84 | 40 | 0.90 | 13 | 1.12 |
| 39 | 0.86 | 26 | 0.90 | 36 | 1.13 |
| 38 | 0.87 | 32 | 0.90 | 11 | 1.14 |
| 10 | 0.88 | 19 | 0.91 | 27 | 1.20 |
| 28 | 0.88 | 41 | 0.92 | 30 | 1.50 U |

Sample B

| | | | |
|---|---|---|---|
| Number of participants | 33 | Range | 0.47 |
| Number of omitted results | 1 | Variance | 0.01 |
| True value | 1.3 | Standard deviation | 0.11 |
| Mean value | 1.3 | Relative Standard deviation | 8.30 % |
| Median value | 1.3 | Relative error | 0.20 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 8 | 1.15 | 5 | 1.26 | 1 | 1.31 |
| 6 | 1.15 | 33 | 1.28 | 41 | 1.31 |
| 35 | 1.20 | 34 | 1.28 | 7 | 1.31 |
| 16 | 1.20 | 19 | 1.28 | 2 | 1.31 |
| 42 | 1.22 | 28 | 1.29 | 29 | 1.31 |
| 21 | 1.23 | 24 | 1.30 | 3 | 1.32 |
| 14 | 1.23 | 27 | 1.30 | 11 | 1.49 |
| 40 | 1.24 | 15 | 1.30 | 13 | 1.50 |
| 39 | 1.25 | 38 | 1.30 | 30 | 1.50 U |
| 10 | 1.26 | 26 | 1.30 | 12 | 1.60 |
| 22 | 1.26 | 32 | 1.31 | 36 | 1.62 |

U = Omitted results

## Table 5. 10. Statistics - Potassium

All methods
Unit: mg/l

Sample A

| | | | |
|---|---|---|---|
| Number of participants | 33 | Range | 0.16 |
| Number of omitted results | 6 | Variance | 0 |
| True value | 0.22 | Standard deviation | 0.03 |
| Mean value | 0.22 | Relative Standard deviation | 14.70 % |
| Median value | 0.22 | Relative error | 1.40 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 21 | < 0.5 U | 24 | 0.22 | 19 | 0.23 |
| 2 | < 0.45 U | 7 | 0.22 | 5 | 0.23 |
| 1 | 0.03 U | 22 | 0.22 | 16 | 0.24 |
| 28 | 0.14 | 14 | 0.22 | 29 | 0.24 |
| 36 | 0.18 | 6 | 0.22 | 11 | 0.25 |
| 34 | 0.18 | 41 | 0.22 | 13 | 0.27 |
| 8 | 0.20 | 3 | 0.23 | 38 | 0.29 |
| 12 | 0.20 | 32 | 0.23 | 15 | 0.30 |
| 42 | 0.20 | 39 | 0.23 | 33 | 0.34 U |
| 26 | 0.20 | 35 | 0.23 | 30 | 0.40 U |
| 10 | 0.21 | 40 | 0.23 | 27 | 1.20 U |

Sample B

| | | | |
|---|---|---|---|
| Number of participants | 33 | Range | 0.2 |
| Number of omitted results | 6 | Variance | 0 |
| True value | 0.32 | Standard deviation | 0.04 |
| Mean value | 0.32 | Relative Standard deviation | 13.10 % |
| Median value | 0.32 | Relative error | 0.00 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 21 | < 0.5 U | 26 | 0.30 | 39 | 0.35 |
| 2 | < 0.45 U | 14 | 0.31 | 40 | 0.35 |
| 38 | 0.20 | 19 | 0.31 | 16 | 0.35 |
| 13 | 0.25 | 5 | 0.31 | 22 | 0.35 |
| 34 | 0.27 | 24 | 0.32 | 29 | 0.35 |
| 8 | 0.27 | 35 | 0.32 | 36 | 0.38 |
| 33 | 0.29 U | 6 | 0.32 | 11 | 0.38 |
| 12 | 0.30 | 10 | 0.33 | 15 | 0.40 |
| 28 | 0.30 | 41 | 0.34 | 30 | 0.40 U |
| 7 | 0.30 | 3 | 0.34 | 1 | 0.47 U |
| 42 | 0.30 | 32 | 0.34 | 27 | 1.10 U |

U = Omitted results

## Table 5. 11. Statistics - Aluminium

All methods
Unit: Ág/l

Sample C

| | | | |
|---|---|---|---|
| Number of participants | 17 | Range | 75 |
| Number of omitted results | 0 | Variance | 422 |
| True value | 82 | Standard deviation | 21 |
| Mean value | 82 | Relative Standard deviation | 25.00 % |
| Median value | 82 | Relative error | -0.30 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 38 | 47 | 24 | 78 | 22 | 90 |
| 8 | 49 | 5 | 82 | 16 | 95 |
| 3 | 61 | 4 | 82 | 41 | 104 |
| 33 | 65 | 35 | 84 | 14 | 115 |
| 36 | 67 | 32 | 85 | 15 | 122 |
| 42 | 77 | 40 | 86 | | |

Sample D

| | | | |
|---|---|---|---|
| Number of participants | 17 | Range | 86 |
| Number of omitted results | 0 | Variance | 360 |
| True value | 114 | Standard deviation | 19 |
| Mean value | 111 | Relative Standard deviation | 16.60 % |
| Median value | 114 | Relative error | -2.40 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 8 | 59 | 40 | 111 | 32 | 116 |
| 33 | 92 | 24 | 114 | 16 | 118 |
| 38 | 93 | 42 | 114 | 41 | 133 |
| 36 | 103 | 22 | 115 | 14 | 133 |
| 5 | 104 | 3 | 115 | 15 | 145 |
| 4 | 110 | 35 | 116 | | |

U = Omitted results

## Table 5. 12. Statistics - Aluminium, reactive

All methods
Unit: Ág/l

Sample C

| | | | |
|---|---|---|---|
| Number of participants | 9 | Range | 7 |
| Number of omitted results | 5 | Variance | 8 |
| True value | 24 | Standard deviation | 3 |
| Mean value | 24 | Relative Standard deviation | 11.90 % |
| Median value | 24 | Relative error | -1.70 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 38 | 11 U | 24 | 25 | 42 | 54 U |
| 35 | 20 | 5 | 27 | 22 | 80 U |
| 4 | 23 | 8 | 46 U | 20 | 90 U |

Sample D

| | | | |
|---|---|---|---|
| Number of participants | 9 | Range | 20 |
| Number of omitted results | 5 | Variance | 92 |
| True value | 99 | Standard deviation | 10 |
| Mean value | 100 | Relative Standard deviation | 9.70 % |
| Median value | 99 | Relative error | 0.60 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 8 | 50 U | 4 | 93 | 5 | 110 |
| 38 | 77 U | 42 | 100 U | 20 | 115 U |
| 24 | 90 | 35 | 105 | 22 | 150 U |

U = Omitted results

## Table 5. 13. Statistics - Aluminium, nonlabile

All methods
Unit: Ág/l

Sample C

| | | | |
|---|---|---|---|
| Number of participants | 8 | Range | 21 |
| Number of omitted results | 4 | Variance | 85 |
| True value | 50 | Standard deviation | 9 |
| Mean value | 48 | Relative Standard deviation | 18.40 % |
| Median value | 50 | Relative error | -4.00 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 35 | 8 U | 42 | 46 | 4 | 57 |
| 5 | 22 U | 24 | 53 | 20 | 80 U |
| 38 | 36 | 22 | 54 U | | |

Sample D

| | | | |
|---|---|---|---|
| Number of participants | 8 | Range | 12 |
| Number of omitted results | 4 | Variance | 33 |
| True value | 21 | Standard deviation | 6 |
| Mean value | 21 | Relative Standard deviation | 27.30 % |
| Median value | 21 | Relative error | 1.20 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 35 | 12 U | 5 | 23 U | 20 | 40 U |
| 38 | 16 | 24 | 24 | 22 | 43 U |
| 4 | 17 | 42 | 28 | | |

U = Omitted results

## Table 5. 14. Statistics - Dissolved organic carbon

All methods
Unit: mg/l

Sample C

| | | | |
|---|---|---|---|
| Number of participants | 13 | Range | 1.75 |
| Number of omitted results | 0 | Variance | 0.23 |
| True value | 3.72 | Standard deviation | 0.48 |
| Mean value | 3.89 | Relative Standard deviation | 13.00 % |
| Median value | 3.72 | Relative error | 4.60 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 40 | 3.45 | 15 | 3.70 | 5 | 4.22 |
| 41 | 3.50 | 35 | 3.72 | 22 | 4.40 |
| 3 | 3.53 | 42 | 3.80 | 33 | 5.20 |
| 19 | 3.60 | 38 | 3.80 | | |
| 16 | 3.66 | 24 | 4.03 | | |

Sample D

| | | | |
|---|---|---|---|
| Number of participants | 13 | Range | 1.17 |
| Number of omitted results | 0 | Variance | 0.11 |
| True value | 3.25 | Standard deviation | 0.34 |
| Mean value | 3.36 | Relative Standard deviation | 10.40 % |
| Median value | 3.25 | Relative error | 3.50 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 40 | 3.03 | 15 | 3.20 | 5 | 3.49 |
| 3 | 3.04 | 38 | 3.25 | 22 | 3.90 |
| 16 | 3.17 | 19 | 3.30 | 33 | 4.20 |
| 24 | 3.18 | 35 | 3.38 | | |
| 41 | 3.20 | 42 | 3.40 | | |

U = Omitted results

## Table 5. 15. Statistics - Chemical oxygen demand

All methods
Unit: mg/l

Sample C

| | | | |
|---|---|---|---|
| Number of participants | 6 | Range | 2 |
| Number of omitted results | 1 | Variance | 0.69 |
| True value | 4 | Standard deviation | 0.83 |
| Mean value | 4.33 | Relative Standard deviation | 20.70 % |
| Median value | 4 | Relative error | 8.20 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 8 | 1.58 U | 14 | 3.96 | 19 | 4.08 |
| 42 | 3.8 | 4 | 4 | 36 | 5.8 |

Sample D

| | | | |
|---|---|---|---|
| Number of participants | 6 | Range | 0.5 |
| Number of omitted results | 1 | Variance | 0.05 |
| True value | 3.22 | Standard deviation | 0.21 |
| Mean value | 3.2 | Relative Standard deviation | 6.60 % |
| Median value | 3.22 | Relative error | -0.50 % |

Analytical results in ascending order:

| | | | | | |
|---|---|---|---|---|---|
| 8 | 0.63 U | 4 | 3 | 19 | 3.3 |
| 36 | 3 | 14 | 3.22 | 42 | 3.5 |

U = Omitted results

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