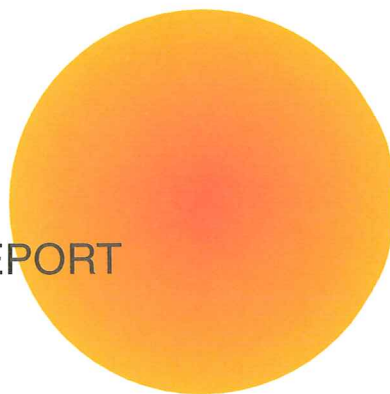


# Convention on Long-range Transboundary Air Pollution

International Cooperative Programme on Assessment and  
Monitoring of Acidification of Rivers and Lakes

ICP-WATERS REPORT



Norwegian Institute for Water Research

56/2000

**Trends in  
intercomparisons  
8701-9812:**

pH, Cond,  $\text{NO}_3 + \text{NO}_2$ , Cl,  $\text{SO}_4$ , Ca,  
Mg, Na, K and aluminium

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Abstract Intercomparison tests connected to the International Cooperative Programme for Monitoring and Assessment of Acidification of Rivers and Lakes, have been organized every year since 1987 by the Programme Centre at Norwegian Institute for Water Research. Sixteen laboratories have participated in six or more intercomparisons. These laboratories were selected for evaluation of possible trends in their performance based on the intercomparison results reported. No clear performance trend for this group of laboratories can be found. A probable reason for this may be that nearly all of these laboratories have been well established for many years, and thus the participation in intercomparisons will have only minor effects on their analytical quality. However, some laboratories show systematically positive or negative deviations from the target value, and should improve the methods used. Others show random deviations from the target value and should improve the internal control routines. During the twelve year period acceptable results have been reported for conductivity from 8 laboratories, nitrate + nitrite from 3, chloride from 6, sulfate from 8, calcium from 10, magnesium from 11, sodium from 2, and potassium from 4 laboratories.
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# CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION

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

### **Trends in intercomparisons 8701 - 9812**

pH, Cond,  $\text{NO}_3^- + \text{NO}_2^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{--}$   
 $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , Al

Prepared by the Programme Centre  
Norwegian Institute for Water Research  
Oslo, October 2000

## Preface

The International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP-Waters) was established under the Executive Body of the Convention on Long-Range Transboundary Air Pollution at its third session in Helsinki in July 1985. The Executive Body has also accepted Norway's offer to provide facilities for the Programme Centre, which has been established at the Norwegian Institute for Water Research, NIVA. A programme subcentre is established at the Laboratory of Freshwater Ecology and Inland Fisheries at University of Bergen. The ICP-Waters programme has been lead by Berit Kvæven, Norwegian Pollution Control Authority.

The Programme objective is to establish an international network of surface water monitoring sites and promote international harmonization of monitoring practices. One of the tools in this work is inter-laboratory quality assurance tests (intercomparisons). The bias between analyses carried out by the individual participants of the Programme has to be clearly identified and controlled.

We here report the possible trends in the analytical performance of participating laboratories from the 12 intercomparison exercises performed so far in this Programme.

Oslo, October 2000

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## Summary

Intercomparisons within the International Cooperative Programme on the Assessment and Monitoring of Acidification of Rivers And Lakes, have been organised annually since 1987, with only minor changes in the analytical programme. The number of participating laboratories has increased from 9 in 1987 to more than 60 in 1998. 16 laboratories have been participating in six intercomparisons or more. These laboratories were selected for evaluation of possible trends in the intercomparison results reported throughout the 12 years.

Generally, there is no clear performance trend for this group of laboratories over this period. A probable reason for this may be that nearly all of these laboratories have analytical experience for many years, and are well equipped. Thus, the participation in intercomparisons will have only minor effects on the analytical quality. However, some laboratories show systematically positive or negative deviations from the target value, and should improve the methods used. Others show random deviations from the target value and should improve the internal control routines. Laboratories reporting results deviating too much from the target values, should increase their effort to find the reason for the deviations, and take measures to improve their performance

The differences between the reported results and the true values have been plotted for ten analytical variables, for each of the 16 laboratories. These plots illustrate the development of the analytical performance at each of the laboratories from 1987 to 1998.

# 1. Introduction

As stated in "Manual for Chemical and Biological Monitoring" (1), between-laboratory quality control is necessary in a 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 intercomparison tests connected to the International Cooperative Programme for Monitoring and Assessment of Acidification of Rivers and Lakes, have been organized yearly by the Programme Centre at Norwegian Institute for Water Research since 1987. With a few exceptions the analytical variables included in the tests have been the same, as shown in Table 2.

## 2. Evaluation of trends

### 2.1 General

Questions have been raised about the possible effect of the intercomparisons, are there any improvements to be observed, or is the analytical quality among the participating laboratories more or less the same through the twelve years period the intercomparisons have been organized? May the intercomparisons organised in this way - without any following-up of the laboratories with the most deviating results - be of any help in improving the analytical quality at the participating laboratories?

**Table 1. Alphabetical list of participating laboratories evaluated in this report. N is the number of intercomparisons the laboratory has participated in.**

Laboratory	Country	N
Amt der Kärntner Landesregierung, Klagenfurt	Austria	6
Bayerische Landesamt für Wasserwirtschaft, München	Germany	12
Centre de Geochimie de la Surface, Strasbourg	France	7
CNR Istituto Italiano di Idrobiologia, Pallanza	Italy	11
Czech Geological Survey, Praha	Czech Republic	8
Environmental Protection Agency, Dublin	Ireland	12
Finland Environment Agency Research Laboratory, Helsinki	Finland	12
Freshwater Fisheries Laboratory, Pitlochry	Scotland	7
Freshwater Institute, Winnipeg, Manitoba	Canada	7
Institute of Environmental Protection, Warszawa	Poland	6
National Environmental Research Institute, Silkeborg	Denmark	7
Norwegian Institute for Water Research, Oslo	Norway	12
Research and Engineering Institute for Environment, Bucharesti	Romania	6
Swedish University of Agricultural Sciences, Uppsala	Sweden	12
University of Maine, Water Research Institute, Orono, Maine	USA	8
US Geological Survey, Denver Colorado	USA	6



Whatever the answers to these questions may be, the results of these intercomparisons are documenting the analytical quality at the participating laboratories which are supporting the international data base, hosted at the Programme Centre, with monitoring data. This will be helpful when the analytical results in the data base are used for the evaluation of the acidification situation at different sampling sites.

The number of participating laboratories have increased from 9 in intercomparison 8701 to more than 60 in intercomparison 9812. Only five laboratories have participated in all twelve tests. Some laboratories have participated now and then, however, most of the laboratories being participants today, have participated five times or less. To evaluate a possible trend throughout the intercomparisons, it was decided to include only the laboratories that have participated six times or more. An alphabetical list of these 16 laboratories is shown in Table 1.

There are numerous ways to illustrate the deviations in the analytical results reported by the laboratories. A plot of the relative deviation from the "true" value is expected to be useful for most of the analytical variables. However, this presupposes that the concentrations of the analytical variables of interest are of comparable magnitude, and being markedly higher than the detection limit of the method used. At low concentrations, and for analytical variables such as pH which is representing the logarithm of the concentration, it may be better to use the absolute magnitude of the deviation from the "true" value. The "true" values of the different analytical variables in all the intercomparisons organised so far are shown in the Table 3. These values have to be brought in mind when the analytical results are evaluated, especially when the concentrations are close to the detection limit of the analytical method used, as this may lead to large relative deviations. From Table 3 we find that the "true" value for certain analytical variables may vary a lot from one intercomparison to another, and this fact must be kept in mind when we are evaluating the analytical results.

To make it easier to compare the results of different laboratories, it was decided to use the same length of the abscissa axis for all the laboratories for a given analytical variable. As some laboratories did not participate in every intercomparison, there may be some missing results along the abscissa axis, and these samples are marked with a cross in the plots. This means that in plots where no column are shown, nor a cross, the laboratory has reported a result being the same as the true value. Some of the columns may be so tall that they are longer than the ordinate axis, these columns are representing results which deviate strongly from the "true" value.

The length of the ordinate axis is kept the same for all laboratories for a given analytical variable, however, the zero point of the ordinate axis is moved up or down to get as many results as possible inside the plot. As "true" value in the intercomparisons we have used the median value of the reported results for a given analytical variable. Therefore we have made plots of the relative difference between the result reported by the laboratory and the "true" value. The deviation calculated this way is plotted against the sample number. For the first sample where this specific variable should be determined in these intercomparisons the sample number is 1, and is increasing during the years. Therefore sample number 1 may be representing different samples for different analytical variables, in Table 3 the sample numbers for all the analytical variables are given in the column called X-axis no.

Table 2. The analytical variables that have been included in intercomparison 8701 - 9812.

Analytical variable	8701	8802	8903	9004	9105	9206	9307	9408	9509	9610	9711	9812
pH	X	X		X	X	X	X	X	X	X	X	X
Conductivity	X	X			X	X	X	X	X	X	X	X
Alkalinity		X		X	X	X	X	X	X	X	X	X
Nitrate + nitrite-N		X			X	X	X	X	X	X	X	X
Chloride		X			X	X	X	X	X	X	X	X
Sulphate	X	X			X	X	X	X	X	X	X	X
Calcium	X	X			X	X	X	X	X	X	X	X
Magnesium		X			X	X	X	X	X	X	X	X
Sodium		X			X	X	X	X	X	X	X	X
Potassium		X			X	X	X	X	X	X	X	X
Dissolved organic carbon					X	X	X	X	X	X	X	X
Chemical oxygen demand			X		X	X	X	X	X	X	X	X
Aluminium						X	X	X	X	X	X	X
Aluminium, reactive			X			X	X	X	X	X	X	X
Aluminium, non-labile			X				X	X	X	X	X	X

**Table 3. The true values of the analytical variables used in the intercomparisons 8701 - 9812, and the numbering of the x-axis of the plots. The two special intercomparisons 8903 and 9004 are not included here.**

Inter-comp.	X-axis no.	pH	Cond	SO4	Ca	X-axis no.	NO3+	NO2	Cl	Mg	Na	K	X-axis no.	Al
8701	1	5,63	27,3	1,00	0,61	1	413,5		1,97	0,62	2,33	1,00		
	2	5,82	29,5	1,20	0,82	2	422,5		2,50	0,69	2,43	0,93	1	275
	3	6,20	25,0	9,00	2,04	3	638		3,30	0,83	7,61	1,42	2	252
	4	6,58	26,9	10,00	2,44	4	518		2,50	0,57	8,79	1,15	3	53
	5	6,73	3,99	6,92	3,20	5	220		1,88	0,46	1,48	0,35	4	40
	6	6,72	4,12	6,93	3,21	6	21,5		2,99	0,51	5,48	0,37	5	296
8802	7	7,24	6,57	6,90	3,21	7	2460		3,31	0,31	1,96	0,19	6	351
	8	7,32	6,21	5,19	2,46	8	960		1,74	0,35	1,29	0,05	7	399
	9	6,60	3,00	5,34	2,72	9	107		3,10	0,35	2,11	0,26	8	148
	10	7,16	5,44	6,89	2,84	10	261		4,80	0,48	2,15	0,40	9	166
	11	3,79	11,0	8,83	0,96	11	149		1,40	0,39	15,20	0,27	10	109
	12	4,42	3,80	5,90	1,71	12	1138		1,00	0,30	3,61	0,27	11	148
9307	13	4,92	3,26	6,20	1,11	13	2841		22,2	3,00	25,7	7,91	12	530
	14	5,38	3,96	6,00	3,05	14	3912		35,4	4,57	52,4	11,8	13	270
	15	7,57	8,20	4,22	3,00	15	57		0,83	0,19	1,20	0,52	14	170
	16	6,53	3,38	3,70	2,01	16	158		0,67	0,83	0,90	0,20	15	82
	17	6,91	23,5	15,6	15,1	17	160		0,70	0,20	0,89	0,22	16	114
	18	6,99	38,0	24,3	19,7	18	187		1,45	0,44	1,30	0,32	17	149
9509	19	5,09	1,80	2,30	0,88	19	105		8,30	1,07	10,00	1,41	18	122
	20	6,07	2,34	5,28	1,59	20	278		6,89	0,61	2,10	0,44	19	100
	21	5,02	13,2	2,77	1,50	21	270		1,90	0,58	1,74	0,36	20	105
	22	7,05	4,00	3,67	5,30	22	210		2,10	0,26	3,40	0,17		
	23	7,05	8,60	7,52	4,74									
	24	6,80	5,45	5,33	3,80									
9610	25	7,24	5,20	4,70	7,22									
	26	6,70	2,74	2,80	1,05									
9711														
9812														

For each of the sixteen laboratories which have participated in six or more of the intercomparisons, one plot for each analytical variable has been prepared. The length of the column in the graph is representing the relative deviation from the "true" value for the different samples. As ordinate has been chosen the general target accuracy of  $\pm 20\%$ , except for pH and conductivity where there has been used a target acceptance limit of 0,2 pH units and 10 %, respectively.

Alkalinity has not been included in this evaluation, because different units have been used from time to time, and the number of participating laboratories has been much lower than for the other analytical variables. Because very few variables were determined in the intercomparison number 8903 (pH and alkalinity) and 9004 (dissolved organic carbon and aluminium fractions), these special intercomparisons are not included in this report.

## 2.2 pH

For this analytical variable the samples no. 1 - 4 are the samples A - D in intercomparison 8701. The target accuracy for pH given in the Manual (1) is  $\pm 0,1$  pH units, however, in all the intercomparisons organized under this Programme, the deviations in the results reported by the participants were far greater than this target value, therefore, as target accuracy in the reports has been used  $\pm 0,2$  pH units. When we compare the pH results for the different laboratories, we find that the variations in the deviations during the twelve years do not change in any marked way for most laboratories. The laboratories number 1, 2, 5, 6, 9, 11 and 13 have reported mainly acceptable results, while there are larger deviations in the results from the other laboratories.

For pH a problem arise since the procedure used by the laboratories are different, and this difference may affect the results in a systematic way. Thus stirring the solution during the measurement of pH will, in many cases, give lower results than measuring in a quiescent solution. The systematic difference may be dependent on pH in the solution and the degree of supersaturation of CO<sub>2</sub> in the solution. These laboratories are usually expected to report results deviating mainly in the negative direction. Even greater differences are observed for laboratories using equilibration of the solution by bubbling it with air containing 350 ppm CO<sub>2</sub>, the deviation being systematically positive, e.g. laboratory no. 12.

The pH value of the sample seems to affect the variability between the laboratories. Thus, by a closer examination of the illustrations we observe greater deviations at many laboratories when the pH value of the sample is around circumneutrality (e.g. samples no. 5 - 10, 15 - 18, and 22 - 26), indicating that the stirring has greater effect in this pH range. The samples 11 - 14 are quite acidic, the pH values bein between 3,5 and 5,0, here the deviations from the "true" value are generally smaller. Even laboratory no. 12, using equilibration of the solutions, have obtained results comparable to the other laboratories, indicating that the equilibrating procedure affects the pH value much less in acidic solutions.

Laboratories which have reported results that are varying in both positive and negative directions in different intercomparisons, may check the routine for the calibration of the instrument. Variations in both directions may also indicate problems with great random errors.

Since the median value has been selected as the “true” value, evaluation of the pH results is more complicated than for other analytical variables, because the three methods used by the participants are differently affecting the measured values in acidic and neutral solutions.

### **2.3 Conductivity**

For conductivity we have used the relative deviation from the “true” value as ordinate in the plots. In the Manual,  $\pm 20\%$  is used as target accuracy for this analytical variable, however, in many of the intercomparison reports  $\pm 10\%$  has been used, because most laboratories are able to determine conductivity quite precisely. The laboratories number 1, 2, 4, 6, 7, 8, 10 and 13 have reported all their results with deviations less than  $10\%$ . The laboratories number 5, 9, 12, and 14, have reported results where only one or two results are outside the  $\pm 10\%$  limit. Laboratories with many results deviating more than  $\pm 10\%$  from the true value, may have problems with the temperature correction of the results, as the conductivity value is increasing with approximately  $2\%$  per degree when the temperature is about  $20\text{ }^{\circ}\text{C}$  in the measuring solution. These laboratories should check if the temperature correction may be a possible explanation for the observed deviations. Incorrect calibration may also lead to greater deviations. Thus laboratory number 3 has reported 9 results outside the  $\pm 20\%$  accuracy limit.

### **2.4 Nitrate + nitrite**

For this analytical variable the target accuracy of  $\pm 20\%$  has been used as the length of the ordinate axis. The laboratories number 5, 9, and 10, have reported all their results within these limits, while the laboratories number 1, 3, 6, 7, 8, 11, 12, and 13, have reported all results except one or two within this limit. Some of these laboratories have reported results only for a few intercomparisons. For the samples no. 6, 9, 15 and 19 there are extra many large relative deviations. The reason is probably that these samples have the lowest concentrations of nitrate + nitrite, the concentrations being about  $100\text{ }\mu\text{g/l}$  or less.

The laboratories with several results outside the  $\pm 20\%$  limits should check the routine calibration procedure. The great relative deviations at lower concentrations may also be compared to the detection limit of the analytical method used.

### **2.5 Chloride**

The target accuracy of  $\pm 20\%$  has been used as the length of the ordinate axis for the evaluation of the chloride results. The laboratories number 1, 5, 9, 10, 12, and 14, have reported all their results within the target accuracy limit. The laboratories number 2, 3, 4, 6, 7, 8, 13, and 15, have reported all their results except one or two within the  $\pm 20\%$  limits. The laboratories with several results outside the  $\pm 20\%$  limits should check the calibration. The great relative deviations at lower concentrations may also be observed when the results are close to the detection limit of the analytical method used.

## 2.6 Sulfate

For the evaluation of this variable too,  $\pm 20\%$  has been used as target accuracy. There are 8 laboratories that have reported all their values within the target accuracy limit, these laboratories are no. 3, 4, 5, 6, 9, 10, 11, and 12. The laboratories no. 2, 8, 13, 14 and 15 have one or two results reported outside the acceptance limits. For one laboratory, no. 16, all the reported results are outside the acceptance limits. This laboratory is probably using an analytical method with too little sensitivity, or is not running a proper quality control system working at the low concentrations normally used for the samples of these intercomparisons.

## 2.7 Calcium

10 laboratories out of 16 have reported all their results within the target accuracy of  $\pm 20\%$ , this includes the laboratories no. 1, 2, 4, 8, 9, 10, 12, 13, 14, and 15. Four laboratories have one or two results outside these limits, no. 5, 6, 7, and 11. Only two laboratories having more deviating results should check the application range for the analytical methods used to see if the sensitivity is good enough for the samples used here. Also it is important to establish a better internal quality control system which would stop reporting very wrong results.

## 2.8 Magnesium

For this analytical variable 11 laboratories (no. 1, 2, 4, 5, 6, 7, 8, 9, 10, 12, and 15) have reported their results inside the target accuracy limit of  $\pm 20\%$ , while two laboratories have one or two results outside these acceptance limits (no. 11 and 14). The remaining three laboratories have reported results of which most are deviating too much from the true value. These laboratories should check the sensitivity and application range for the analytical method used, and if necessary establish a better quality control system.

## 2.9 Sodium

Sodium results are more spread, only laboratories no. 8 and 13 have reported all their results within the target accuracy limit of  $\pm 20\%$ . One of these laboratories (no. 8) even had all its results within an accuracy limit of  $\pm 5\%$  ! The remaining laboratories, except one, had reported one or two results outside the acceptance limits.

## 2.10 Potassium

For potassium the overall picture is a little different from what we have seen for the other analytical variables, probably because the concentration of this element in the test solutions has been considerably lower, and therefore closer to the detection limit. Thus the four laboratories no. 7, 9, 13, and 15, reported all their results within the target limit of  $\pm 20\%$ . The four laboratories no. 1, 4, 5, and 8, had one or two results outside these limits.

## 2.11 Aluminium

The picture is not always clear for this analytical variable. Laboratory no. 10 reported all results within the accuracy limits, however, they reported results for aluminium only once. The laboratories no. 1, 4, 5, and 7, reported one or two results outside these limits. For this variable generally less results have been reported, and the spreadout of the individual results may probably be caused by the relatively low concentrations used in some of the test solutions. In addition we have to take into consideration that different methods for the determination of this variable have been used, thus affecting the results. For the laboratories no. 11 and 16 there is a dominating trend towards too low results. In all other cases the results are more spread.

## 3. Discussion and conclusions

Generally, there is no clear trend in the performance for the chosen group of laboratories. A highly probable reason for this may be that most of these laboratories have been well established for many years, the staff being highly qualified and the laboratory well equipped with advanced instruments. Thus, the participation in intercomparisons will have only minor effects on the analytical quality. However, there are also examples of poor analytical performance. These laboratories must increase their effort to find the reason for the greater deviations from the target values.

The laboratories evaluated in this report are expected to represent a group of laboratories that have long analytical experience, and are well equipped with modern instruments. Therefore, the conclusion might have been different if we had included all the laboratories in the trend evaluation, i.e. also the laboratories that have participated in the last few intercomparisons only. The yearly meeting of the member countries of ICP Waters has to decide whether these laboratories should be included in a future trend analysis report, or not. The present report is meant to be a help to those laboratories more regularly participating in these intercomparisons, and the plots will indicate where improvements can be made.

The deviations between the reported results and the true values have been plotted for ten analytical variables, and for every one of the sixteen laboratories. These figures illustrate how the laboratories performed throughout this periode of time. These illustrations may be used by each laboratory to identify weaknesses in their methodologies and to improve the analytical quality in the cases where there are too large deviations from the target value. Typical examples for this situation are demonstrated by the laboratories which have a domination of systematically high or systematically low results throughout the twelve years periode.

Another example is given by greater variations in the random errors which is found for some laboratories. In these cases the laboratories should improve their daily quality control. A special case is the random error varying from one intercomparison to another, affecting the results in such a way that all results for a certain parameter in one intercomparison are systematically high or low, and at the next intercomparison quite different. In these cases there should be put an emphasis on the calibration of the analytical equipment.

For some analytical variables there is a problem that the methods and procedures used by the laboratories are giving systematically different results. In such cases the "true" value, which is the median value of the results reported by all the participants, is not representative for the laboratories. One possible solution is to define a reference method for each analytical variable, and the results from the laboratories using this method is used for the determination of the "true" value. Another alternative could be to determine a "true" value for each method. In this case the evaluation would be empirical and connected to one method only. The first alternative should be recommended.

This situation is well demonstrated for pH where three different methods are used. About half of the participants are determining pH in quiescent solution, and the other half of the laboratories are reading the pH value during stirring the solution. The second method is giving somewhat lower results than the first one, especially in samples supersaturated with CO<sub>2</sub>, a situation we often meet in surface water samples. A third method used by only a few laboratories is based on equilibration of the sample before reading the pH value. The results obtained using this method are much higher than the two others, the difference being much smaller when the samples are more acidic.

The results for aluminium fractions are also strongly dependent on the analytical conditions used during the determination, however, this analytical variable is not evaluated in this report.

For the other analytical variables determined in the intercomparisons, a varying number of participants have obtained acceptable results for all the results for a certain variable during the whole period evaluated in this report. For instance, all the results for conductivity reported during the twelve year period are evaluated as acceptable for 8 laboratories, for nitrate + nitrite 3 laboratories, chloride 6, sulfate 8, calcium 10, magnesium 11, sodium 2, and potassium 4. However, it should be kept in mind that very few laboratories have participated in all the intercomparisons in ICP Waters since 1987. Except for conductivity where a narrower acceptance limit of  $\pm 10\%$  has been used, the general acceptance limit has been  $\pm 20\%$ , in accordance with the Manual (1).

For variables where all the reported results from a great number of laboratories are evaluated acceptable, it should be discussed whether the target acceptance limit should be more narrow than today ( $\pm 20\%$ ), for instance  $\pm 15\%$  or  $\pm 10\%$ . Such graduation of acceptance limits takes into consideration that the precision of analytical methods in fact are different. This is the reason for using  $\pm 10\%$  limits for conductivity.

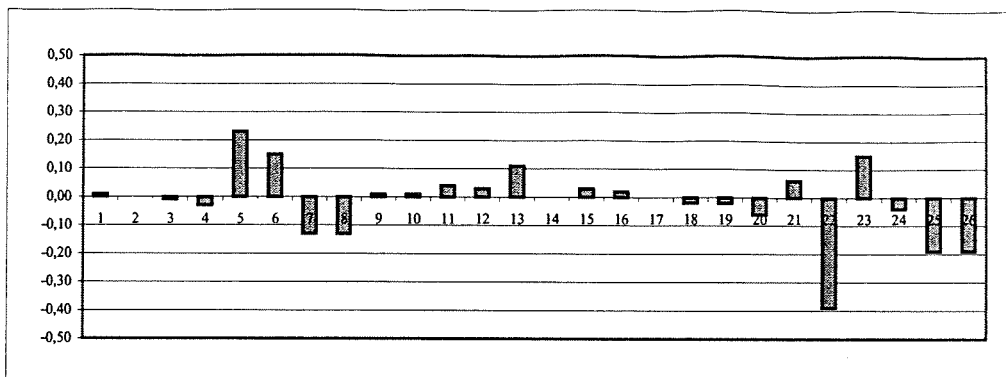
Natural waters are used as basis for the preparation of test samples in the intercomparisons of ICP Water, therefore we may find situations where the analyte concentration is close to the detection limit of the analytical method used. Then the relative uncertainty may be greater than the target accuracy given in the Manual (1), which usually is  $\pm 20\%$  of the "true" value. Therefore, it would be a benefit if there is defined a limit of detection to be obtained for the analytical methods used for the determination of actual variables in this Programme.

In addition, an absolute value to be used for target accuracy in the lower concentration range should be defined. This is necessary if the concentration of the intercomparison samples is in this lower range. Alternatively, it may be decided that the lowest concentration of the test samples should not be lower than a certain distance above the detection limit of the method,

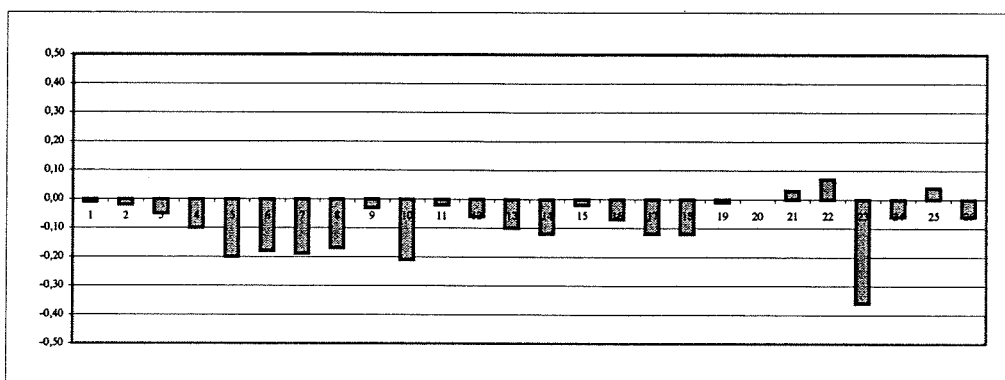


for instance five times the detection limit value. A decision about this should be taken by the steering group.

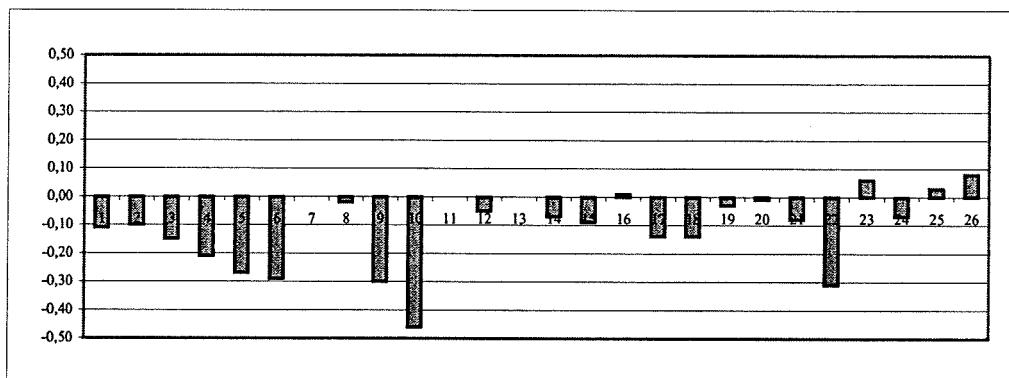
**pH, Laboratory 1**



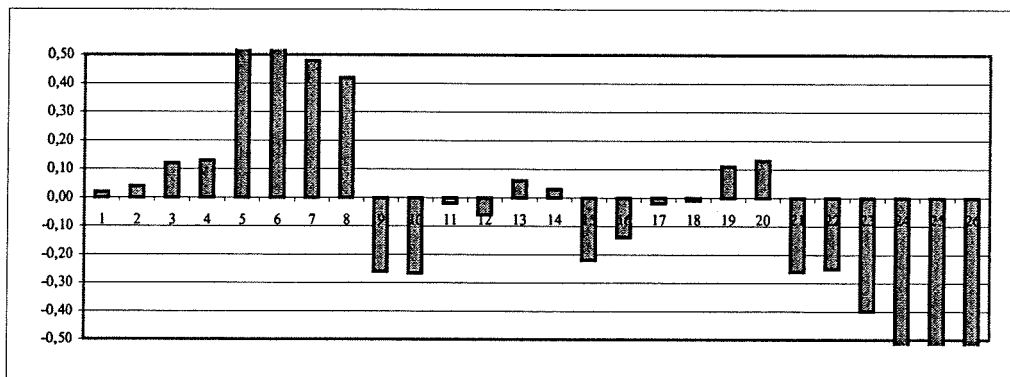
**pH, Laboratory 2**



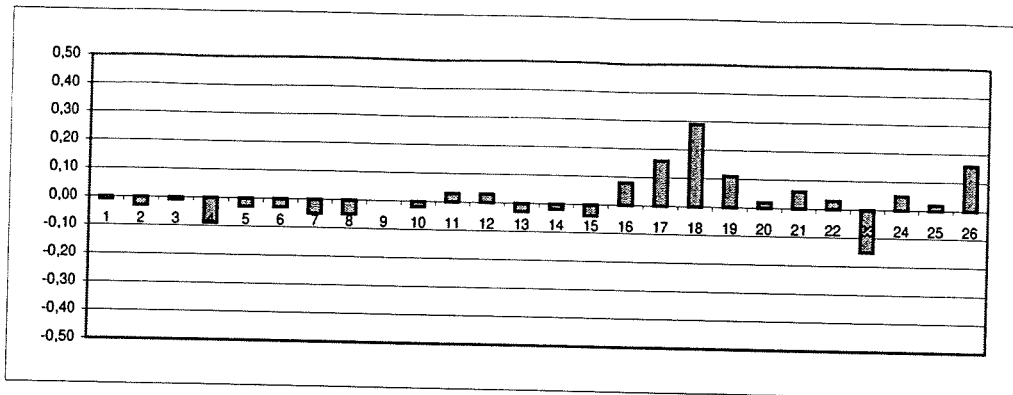
**pH, Laboratory 3**



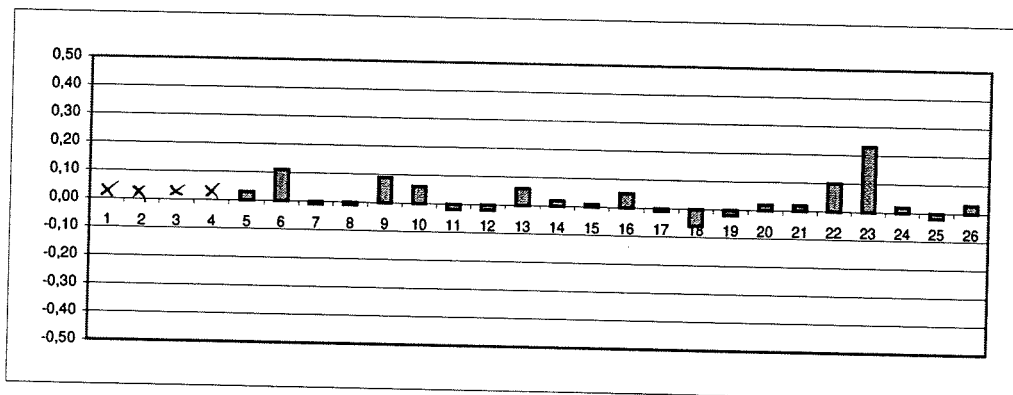
**pH, Laboratory 4**



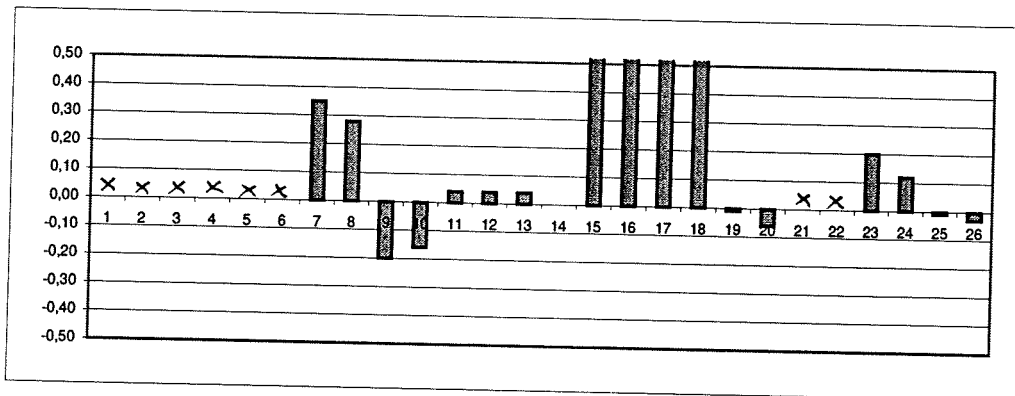
**pH, Laboratory 5**



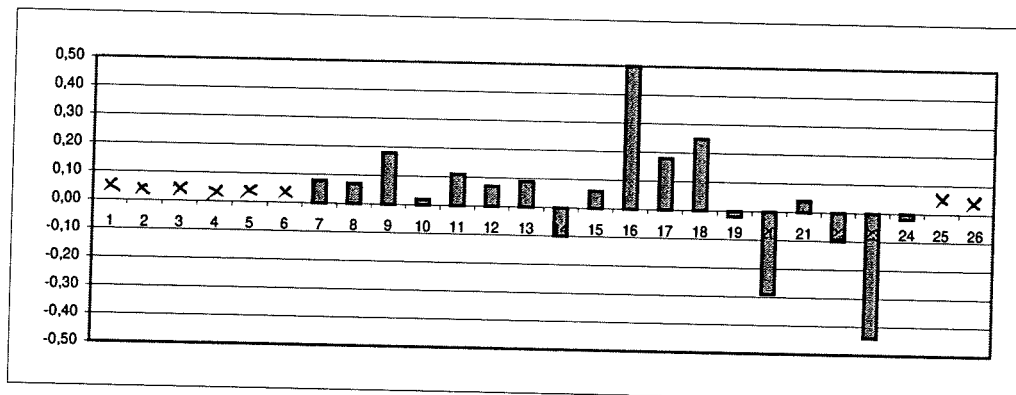
**pH, Laboratory 6**



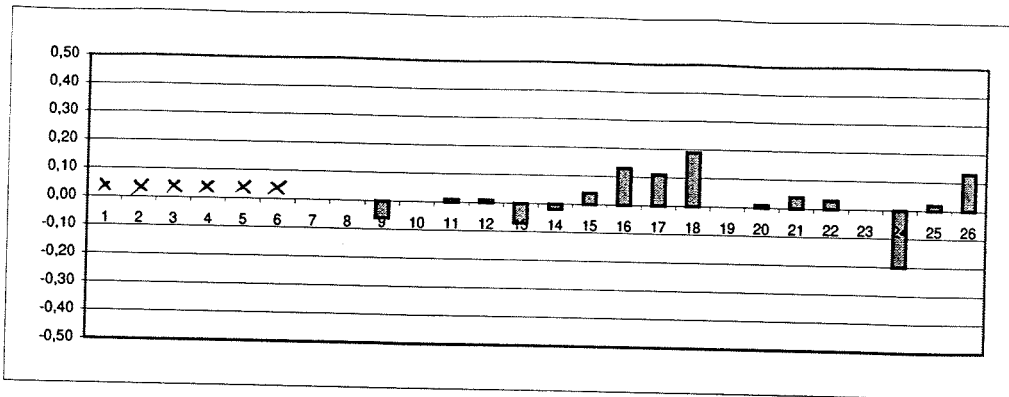
**pH, Laboratory 7**



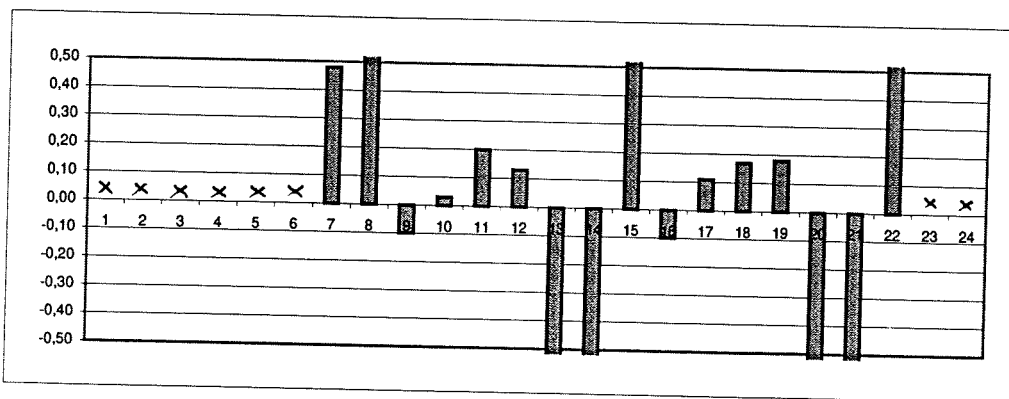
**pH, Laboratory 8**



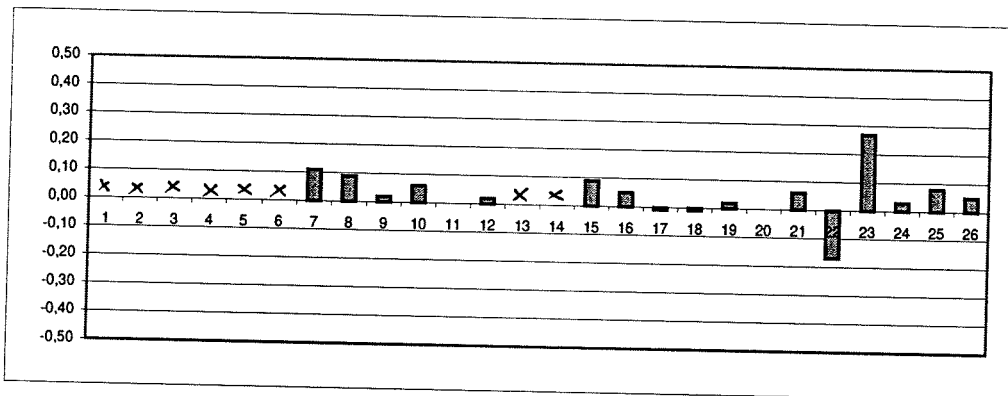
**pH, Laboratory 9**



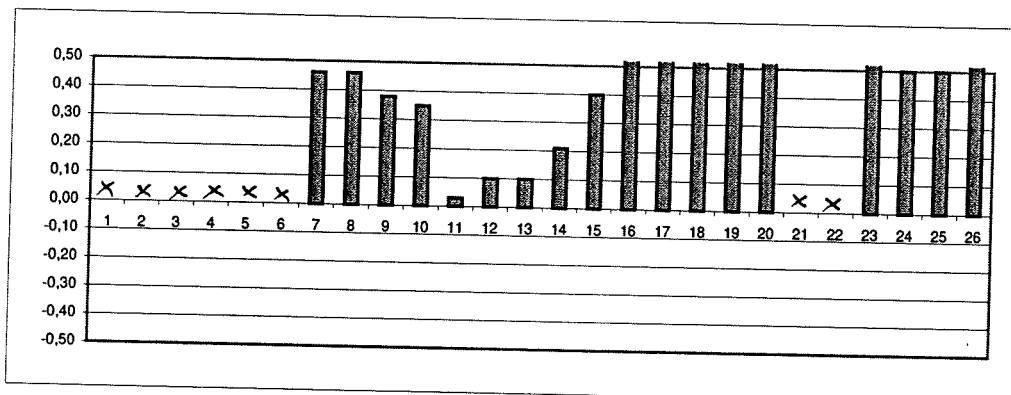
**pH, Laboratory 10**



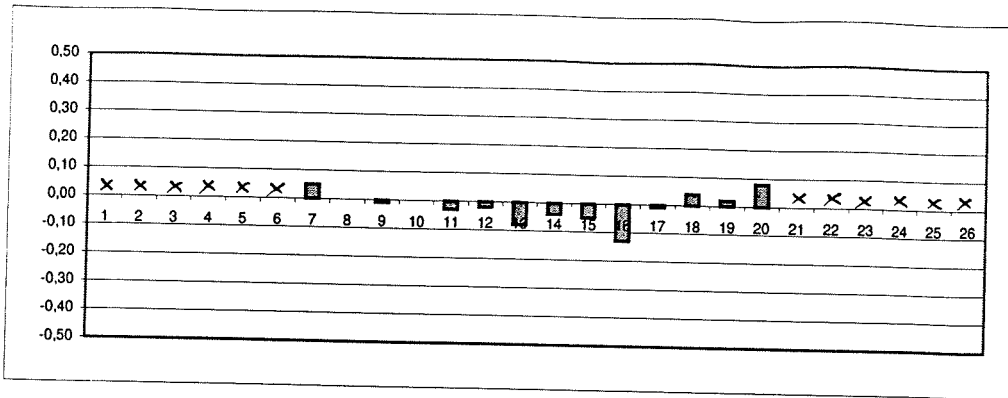
**pH, Laboratory 11**



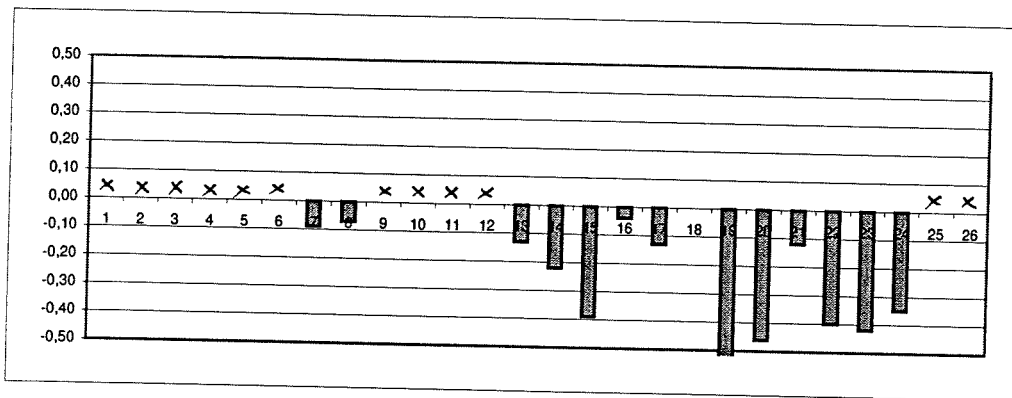
**pH, Laboratory 12**



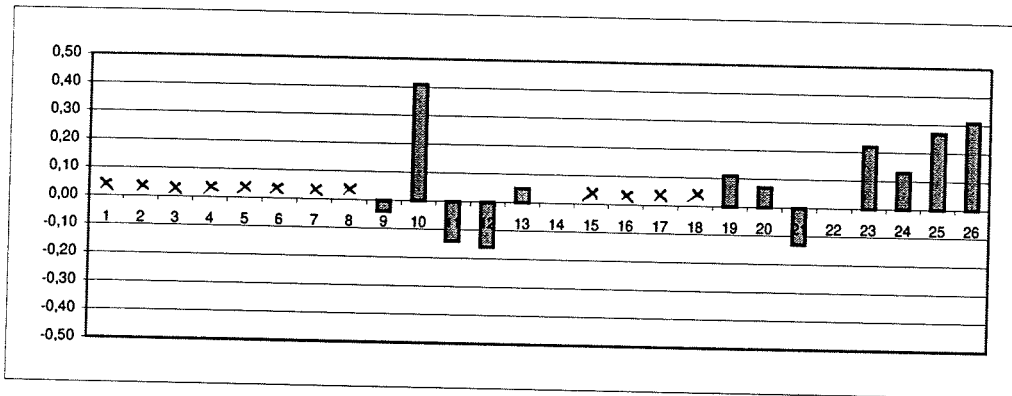
**pH, Laboratory 13**



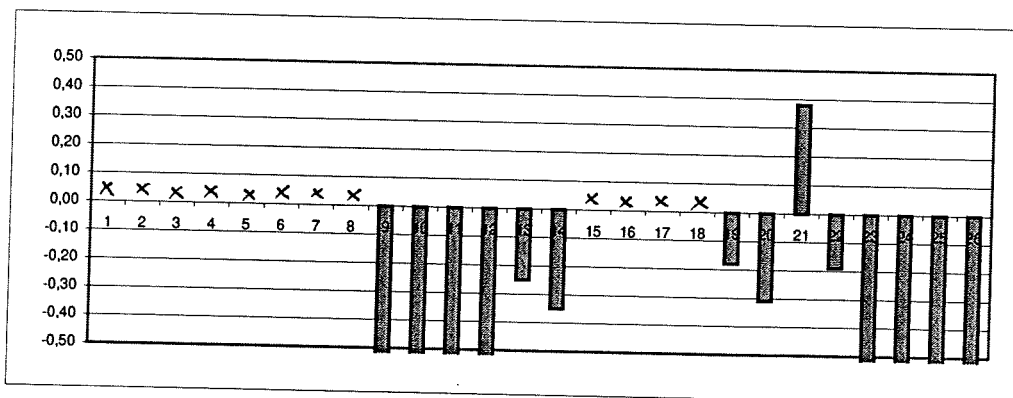
**pH, Laboratory 14**



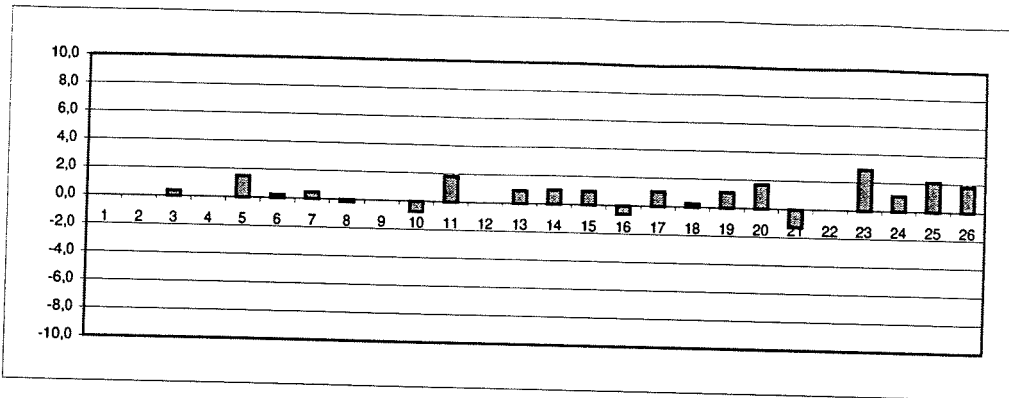
**pH, Laboratory 15**



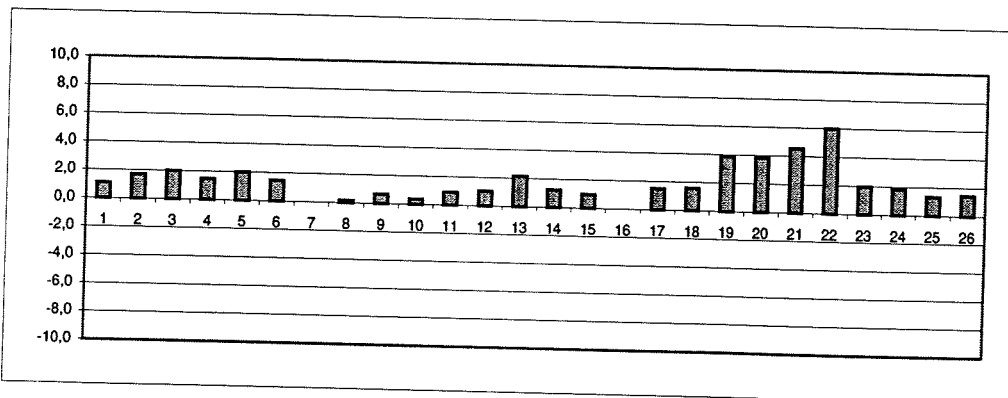
**pH, Laboratory 16**



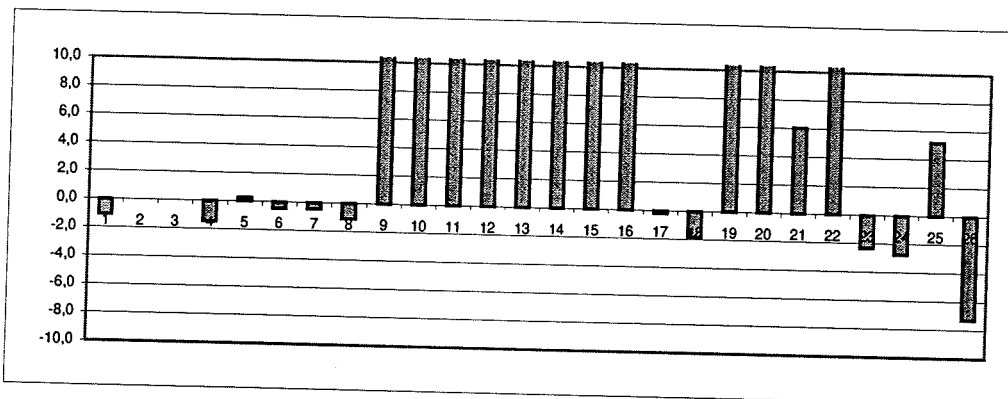
**Conductivity, % relative deviation. Laboratory 1**



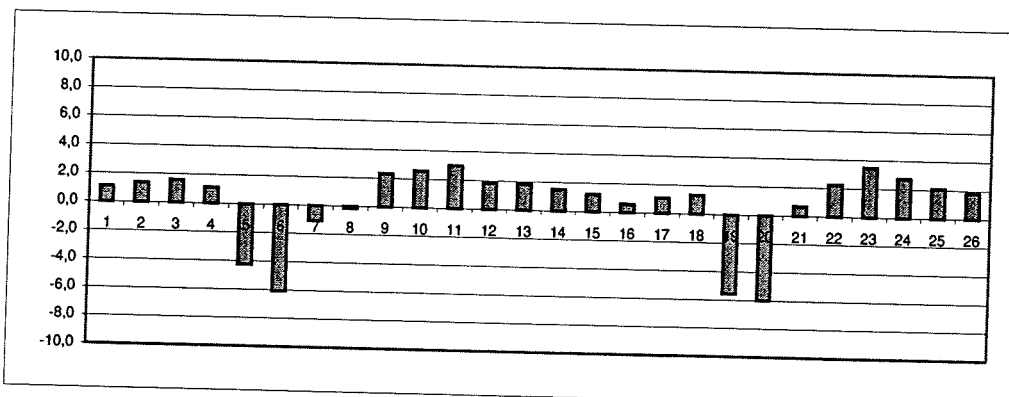
**Conductivity, % relative deviation. Laboratory 2**



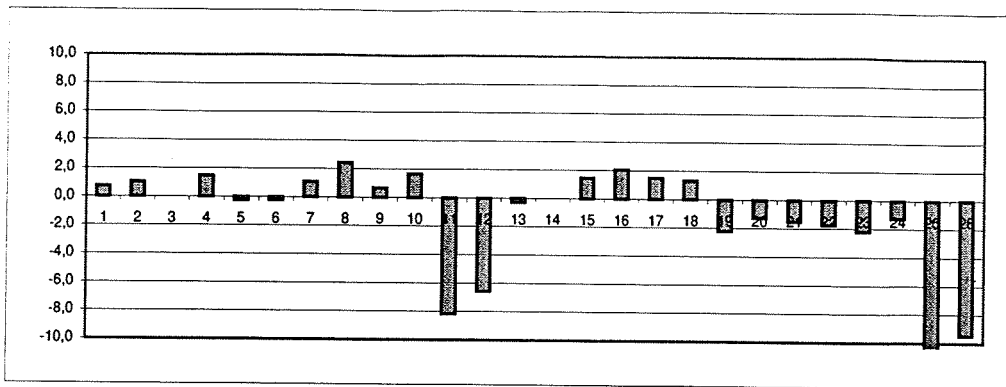
**Conductivity, % relative deviation. Laboratory 3**



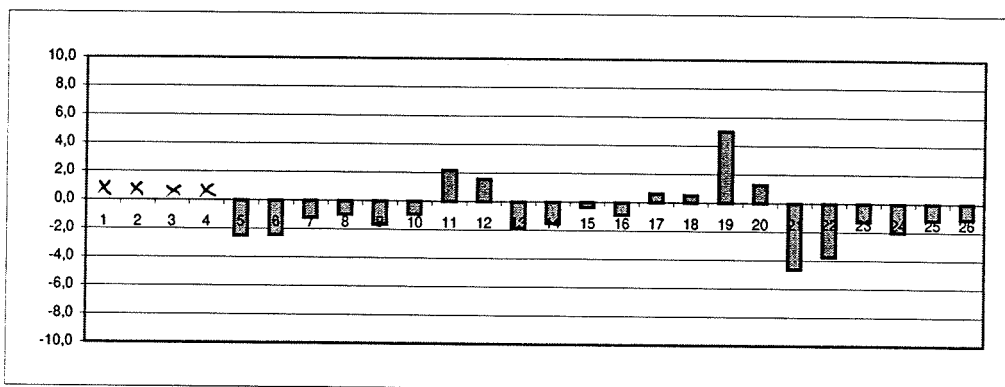
**Conductivity, % relative deviation. Laboratory 4**



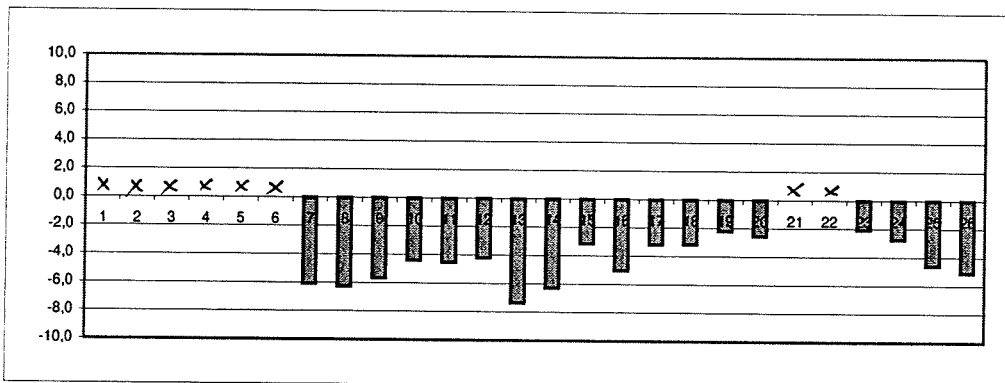
Conductivity, % relative deviation. Laboratory 5



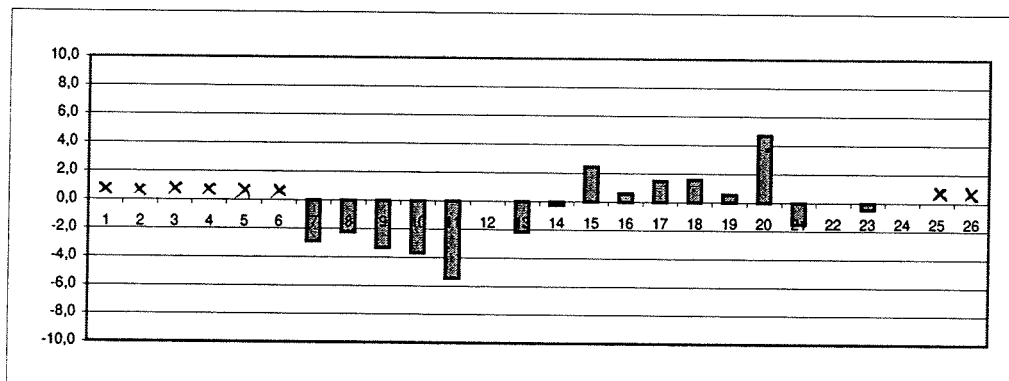
Conductivity, % relative deviation. Laboratory 6



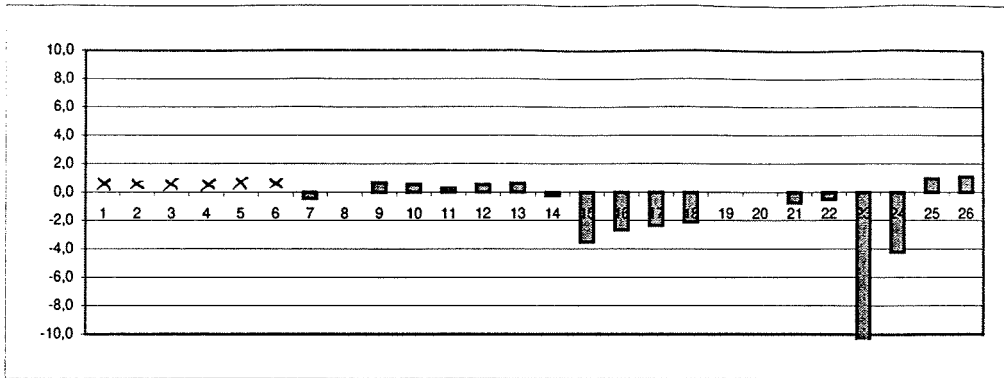
Conductivity, % relative deviation. Laboratory 7



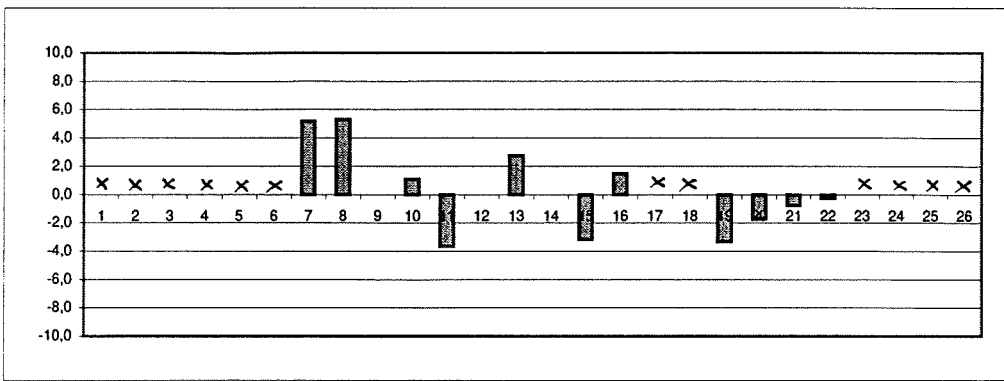
Conductivity, % relative deviation. Laboratory 8



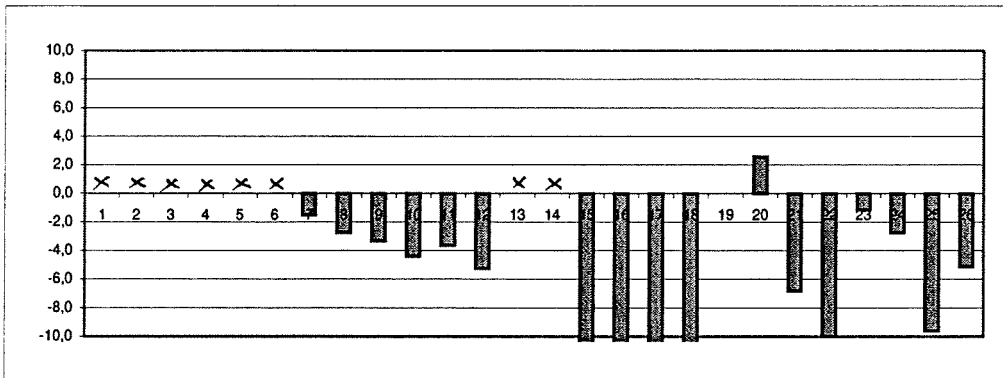
**Conductivity, % relative deviation. Laboratory 9**



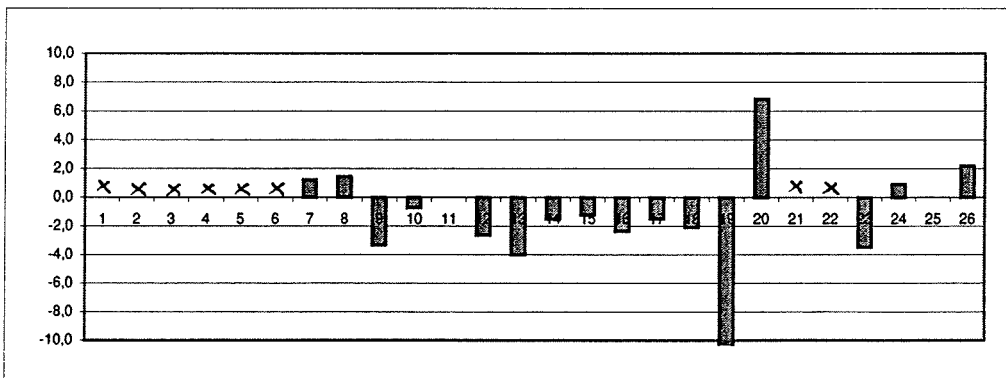
**Conductivity, % relative deviation. Laboratory 10**



**Conductivity, % relative deviation. Laboratory 11**

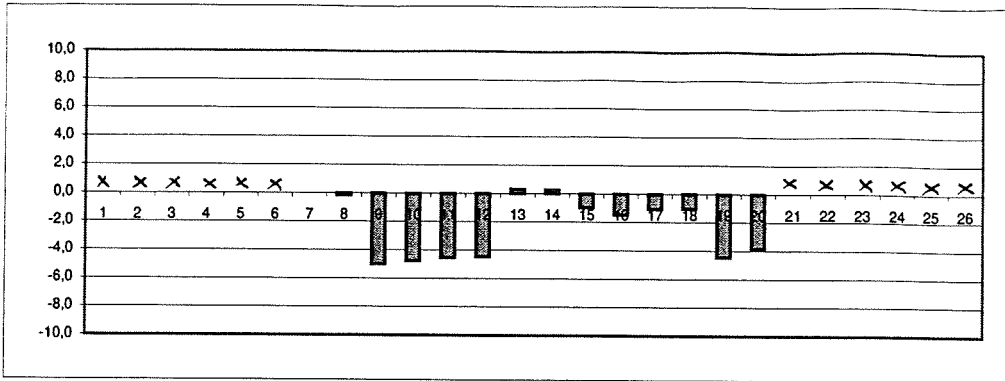


**Conductivity, % relative deviation. Laboratory 12**

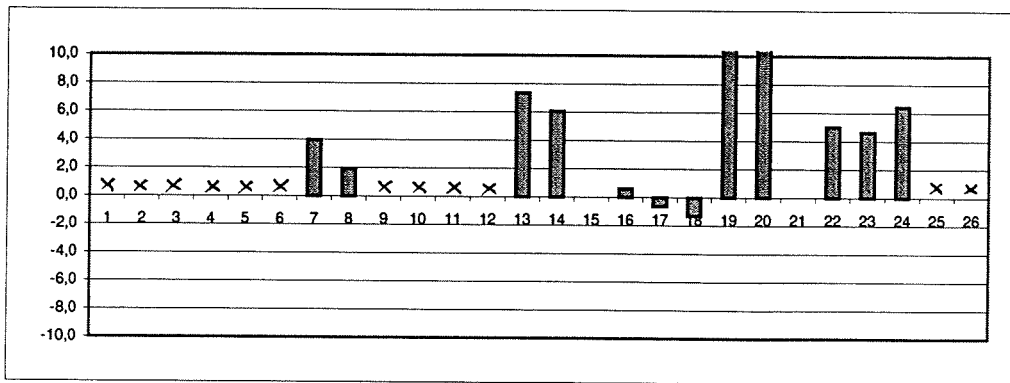




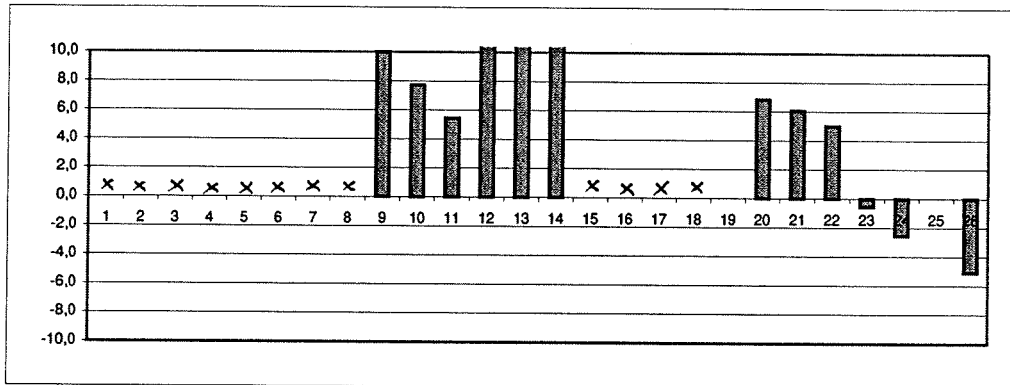
**Conductivity, % relative deviation. Laboratory 13**



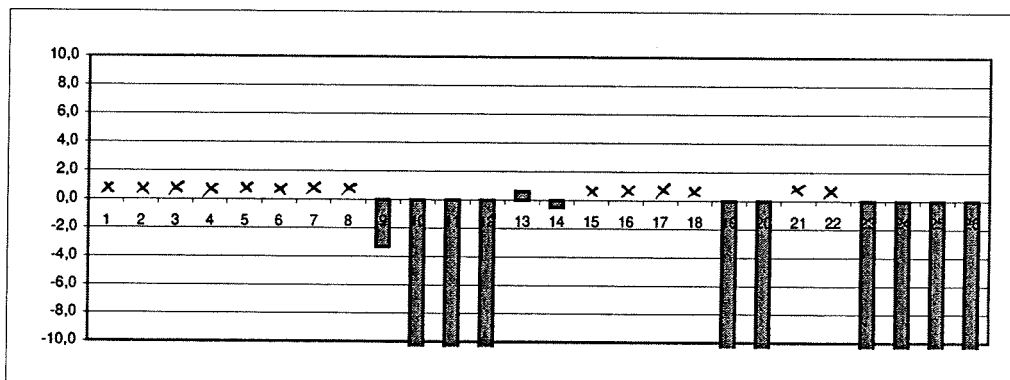
**Conductivity, % relative deviation. Laboratory 14**



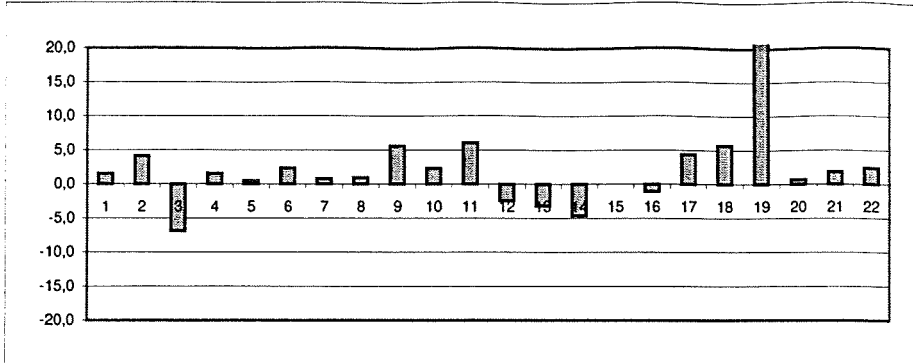
**Conductivity, % relative deviation. Laboratory 15**



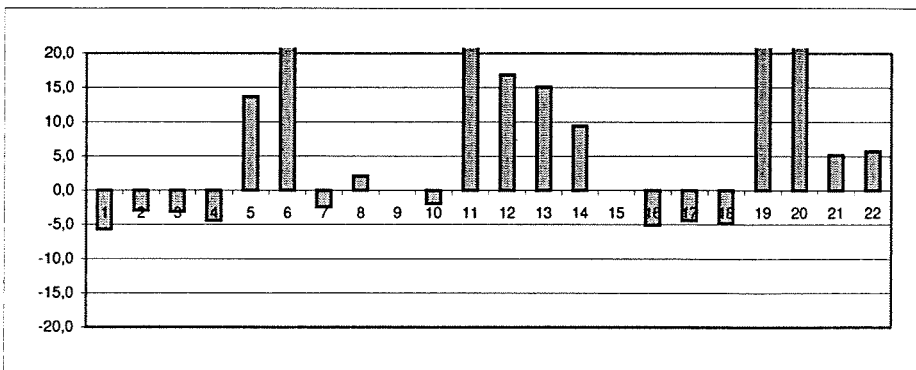
**Conductivity, % relative deviation. Laboratory 16**



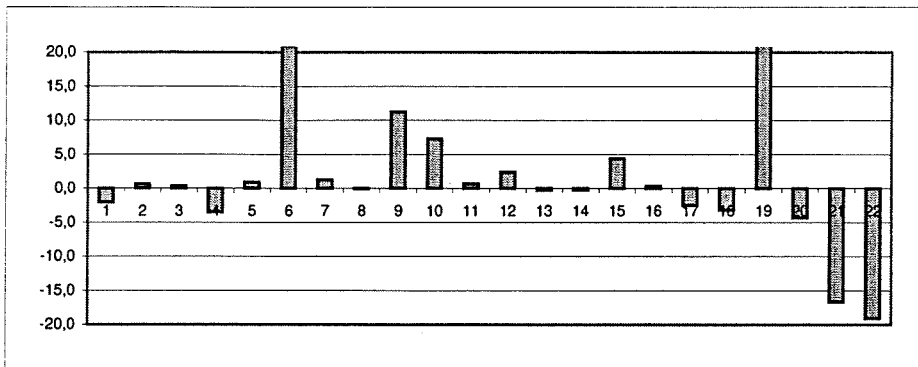
**Nitrate+nitrite, % relative deviation. Laboratory 1**



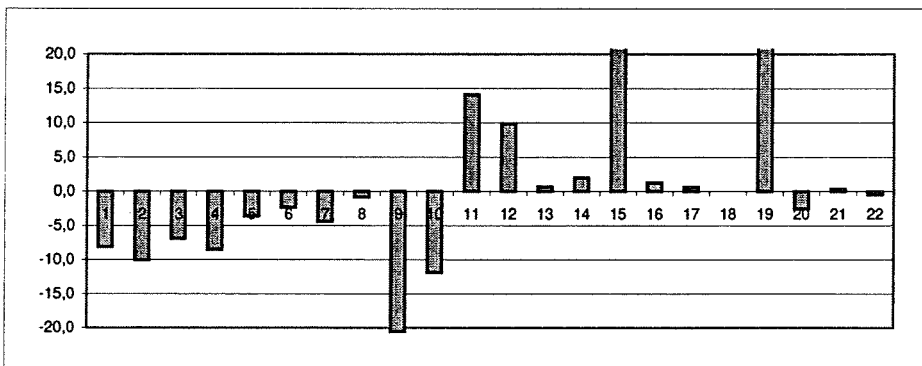
**Nitrate+nitrite, % relative deviation. Laboratory 2**



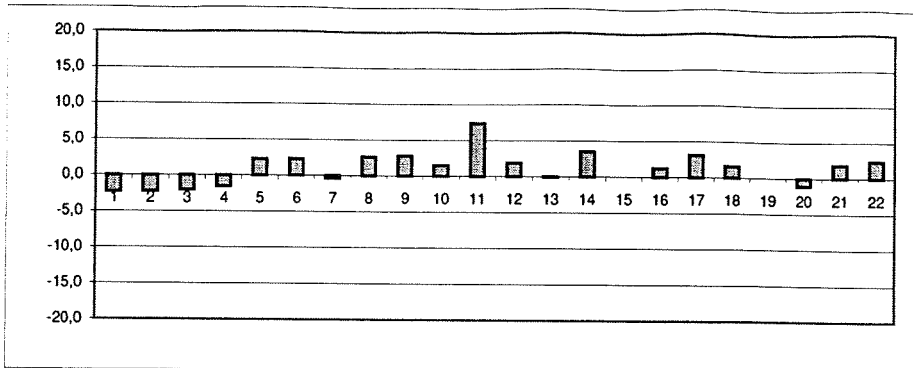
**Nitrate+nitrite, % relative deviation. Laboratory 3**



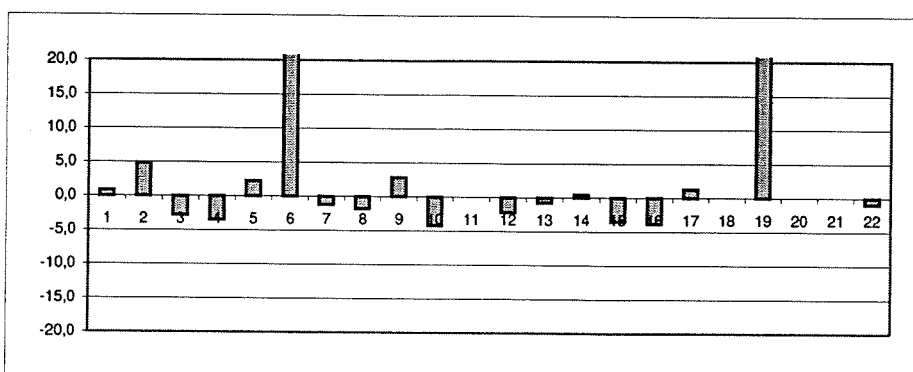
**Nitrate+nitrite, % relative deviation. Laboratory 4**



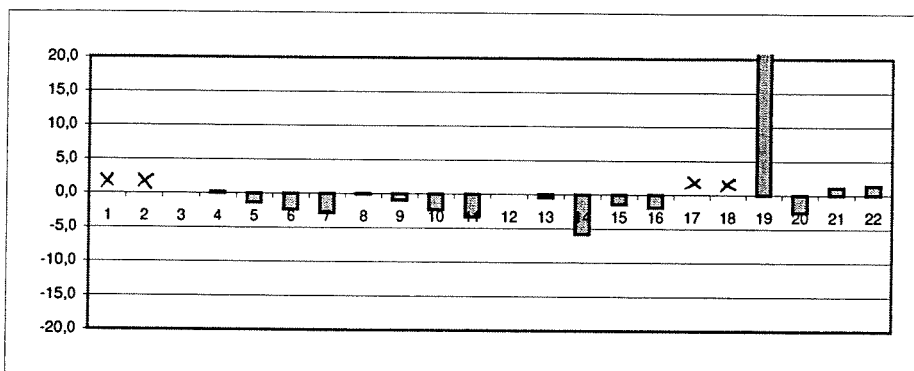
Nitrate+nitrite, % relative deviation. Laboratory 5



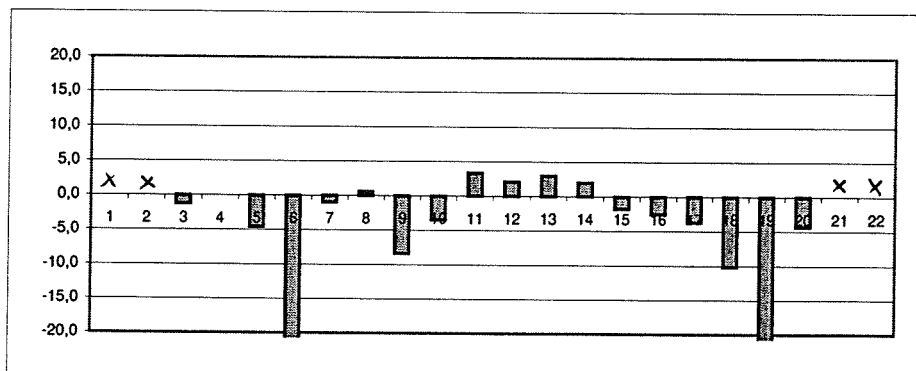
Nitrate+nitrite, % relative deviation. Laboratory 6



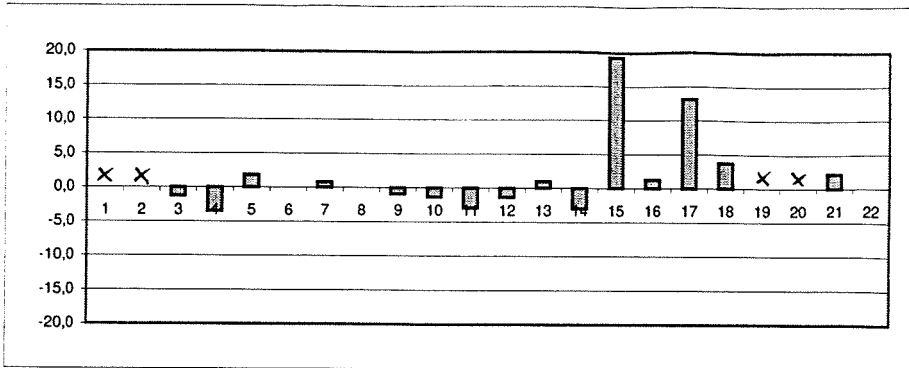
Nitrate+nitrite, % relative deviation. Laboratory 7



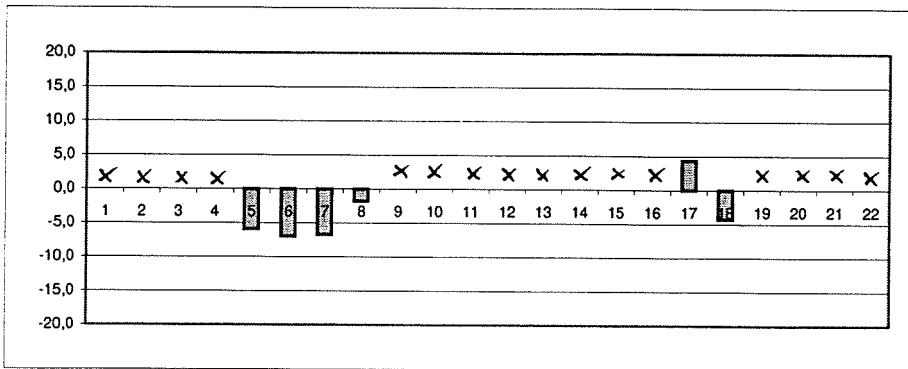
Nitrate+nitrite, % relative deviation. Laboratory 8



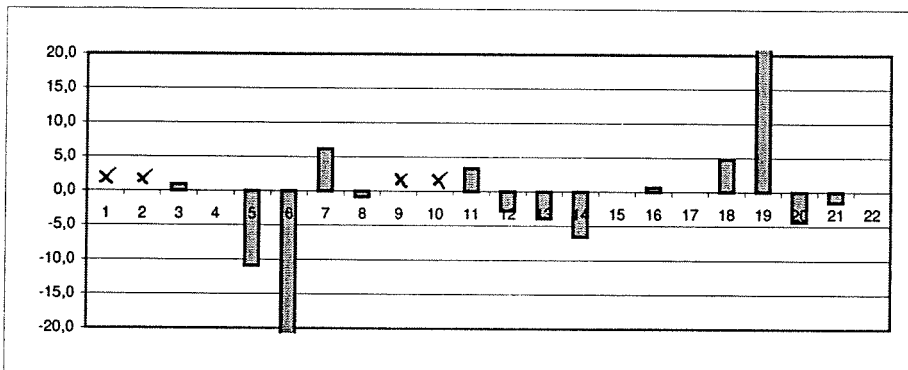
Nitrate+nitrite, % relative deviation. Laboratory 9



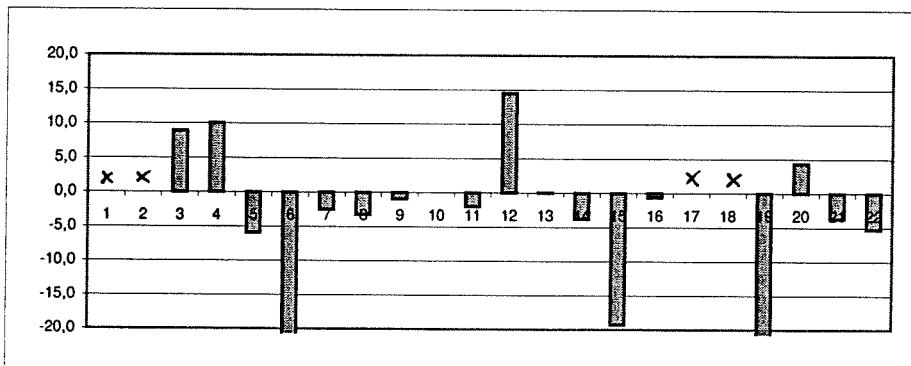
Nitrate+nitrite, % relative deviation. Laboratory 10



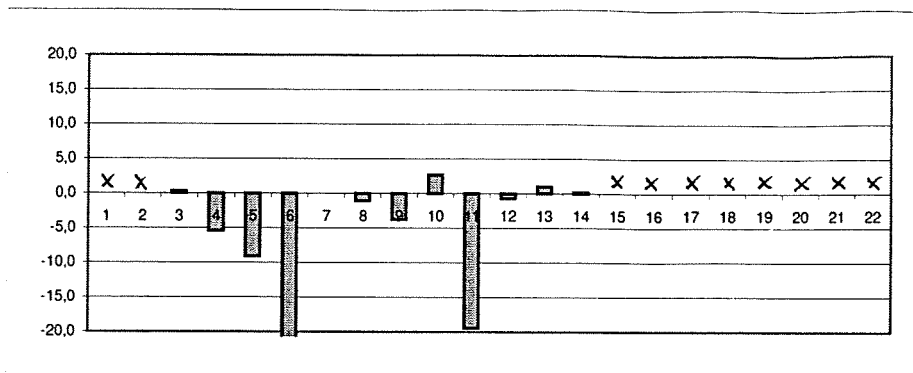
Nitrate+nitrite, % relative deviation. Laboratory 11



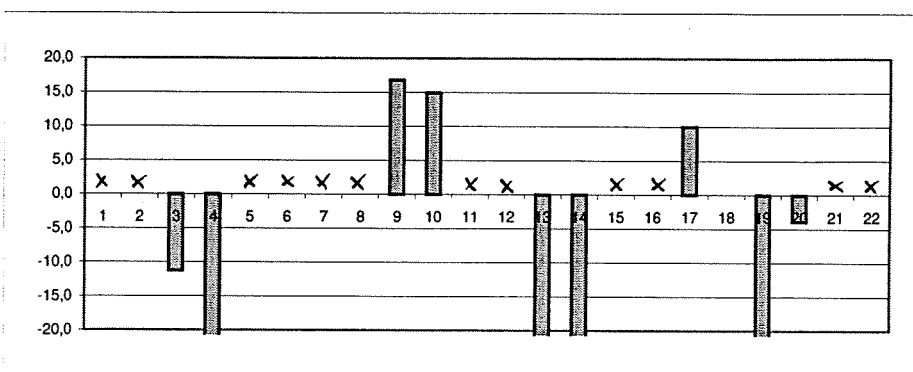
Nitrate+nitrite, % relative deviation. Laboratory 12



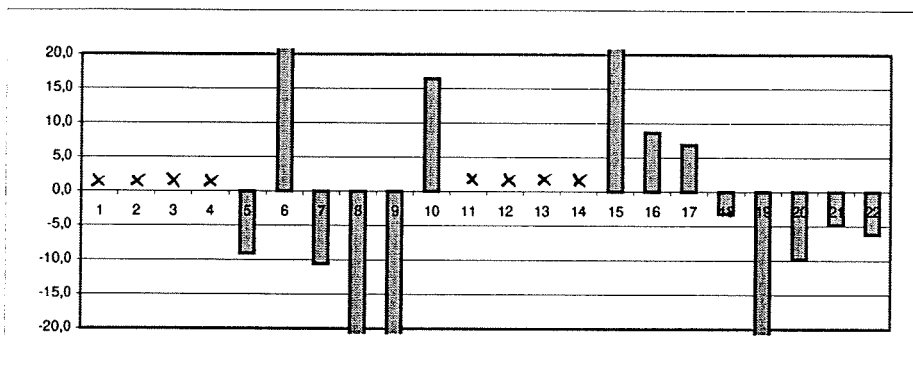
Nitrate+nitrite, % relative deviation. Laboratory 13



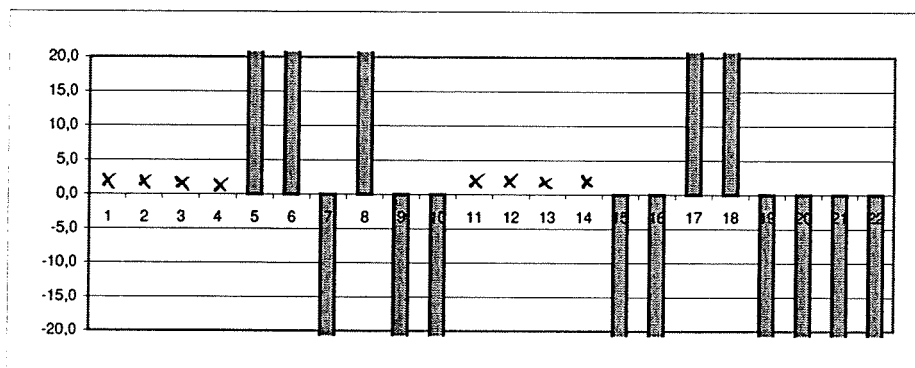
Nitrate+nitrite, % relative deviation. Laboratory 14



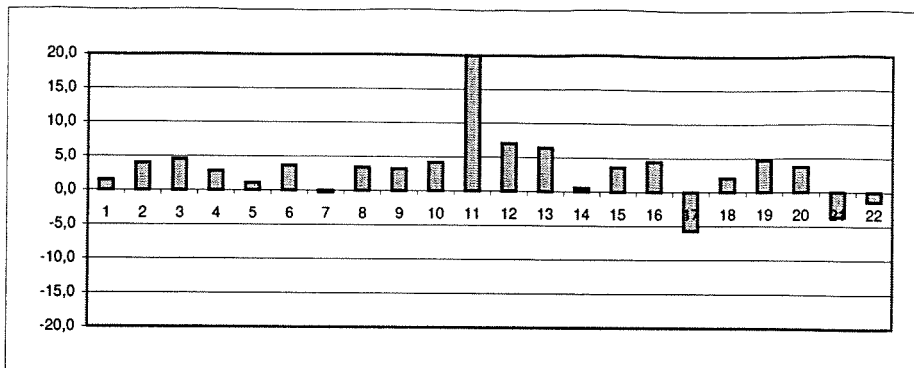
Nitrate+nitrite, % relative deviation. Laboratory 15



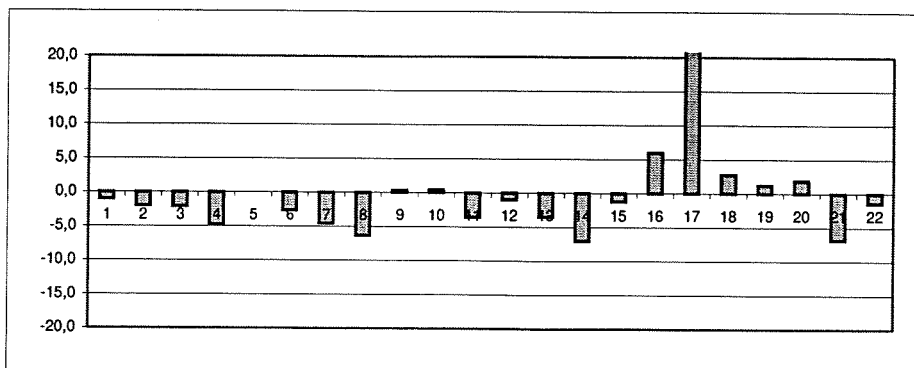
Nitrate+nitrite, % relative deviation. Laboratory 16



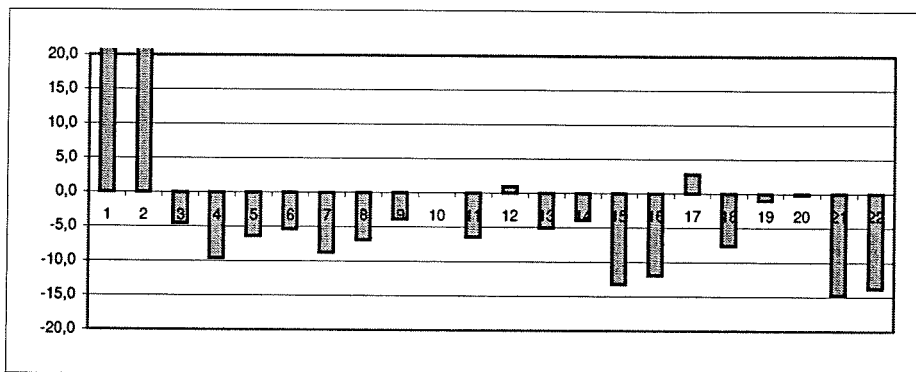
**Chloride, % relative deviation. Laboratory 1**



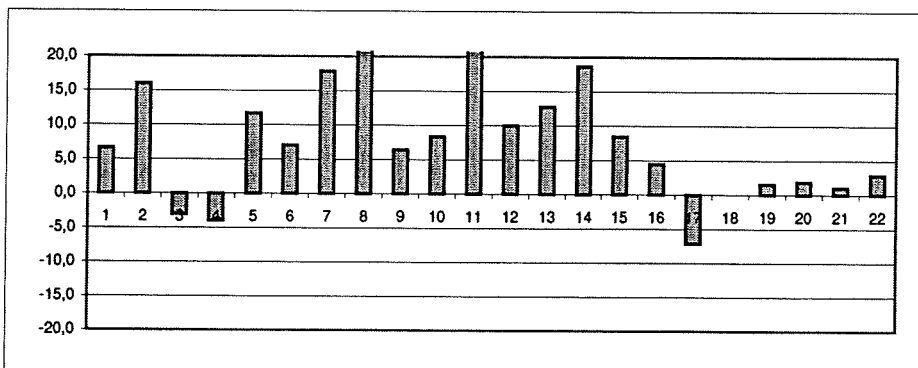
**Chloride, % relative deviation. Laboratory 2**



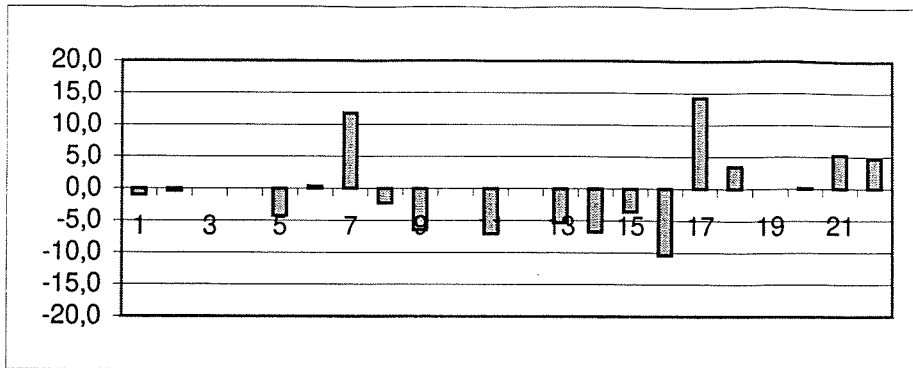
**Chloride, % relative deviation. Laboratory 3**



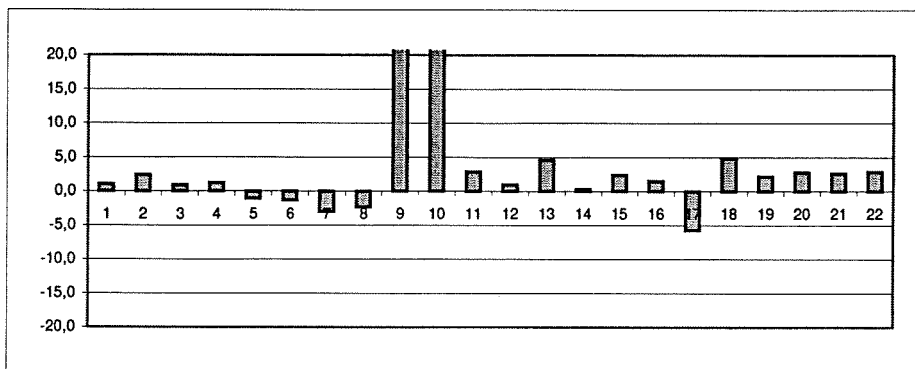
**Chloride, % relative deviation. Laboratory 4**



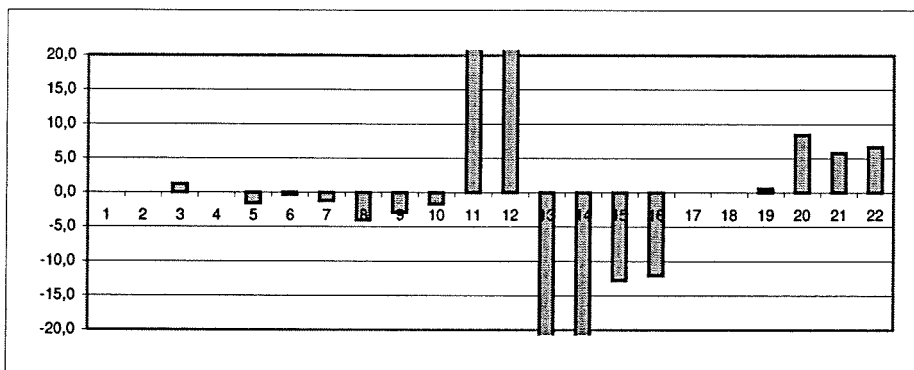
**Chloride, % relative deviation. Laboratory 5**



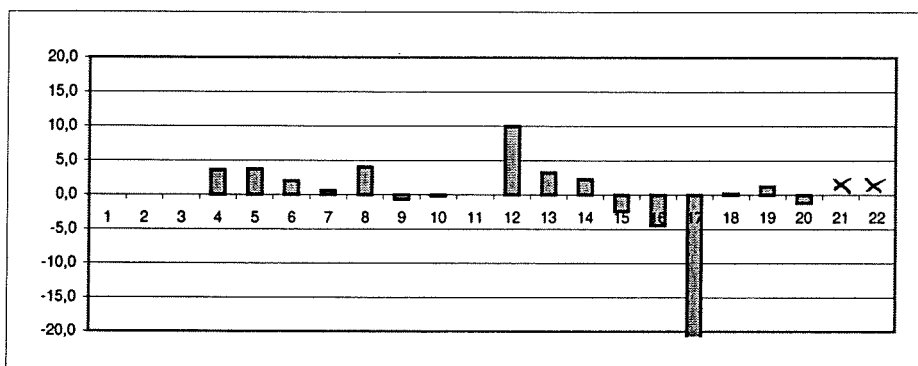
**Chloride, % relative deviation. Laboratory 6**



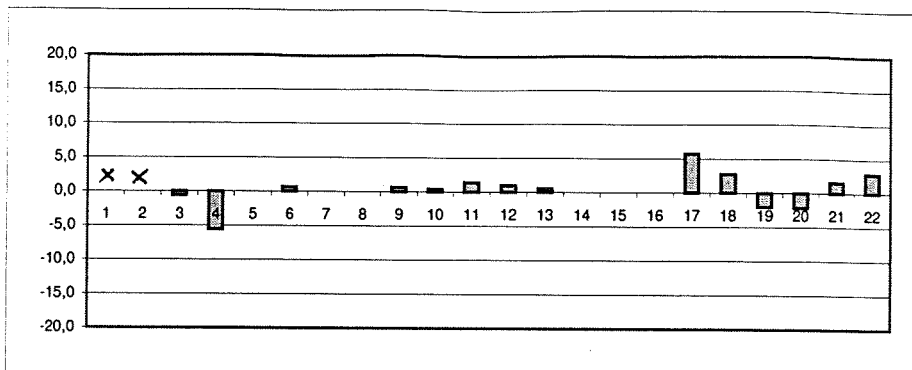
**Chloride, % relative deviation. Laboratory 7**



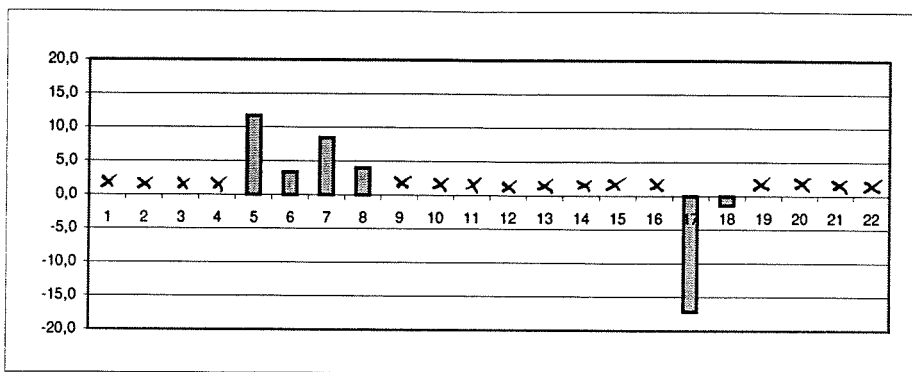
**Chloride, % relative deviation. Laboratory 8**



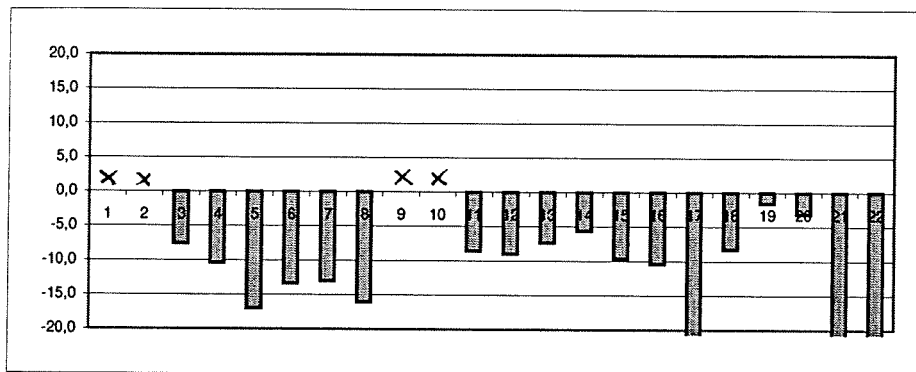
**Chloride, % relative deviation. Laboratory 9**



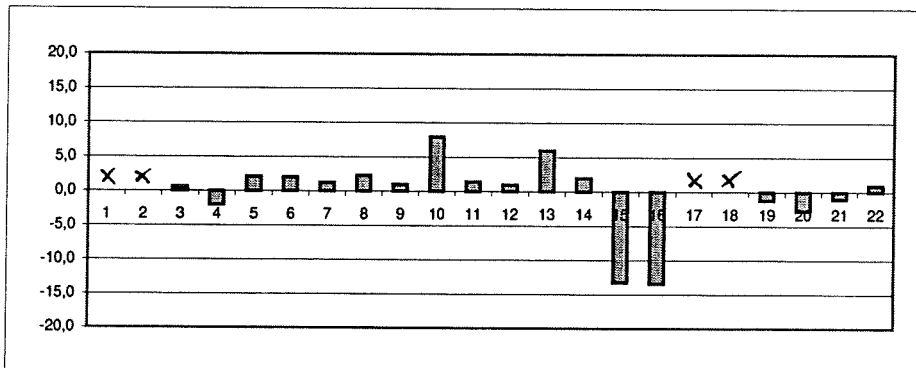
**Chloride, % relative deviation. Laboratory 10**



**Chloride, % relative deviation. Laboratory 11**

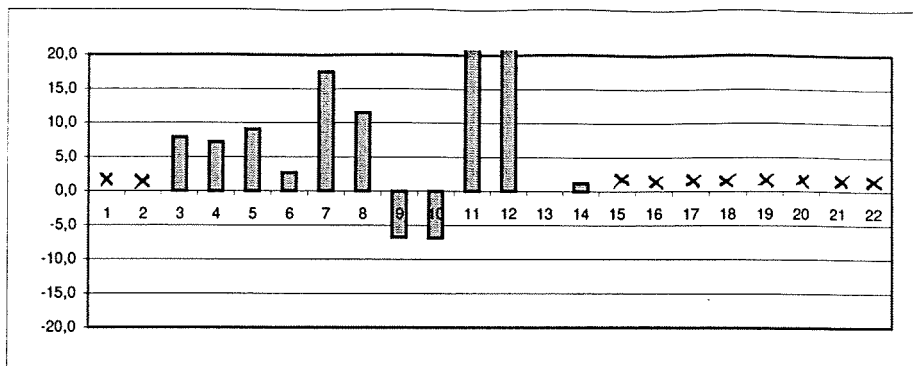


**Chloride, % relative deviation. Laboratory 12**

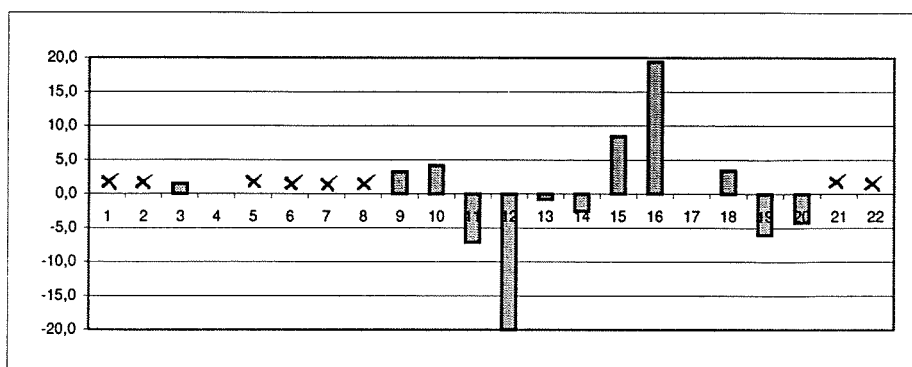




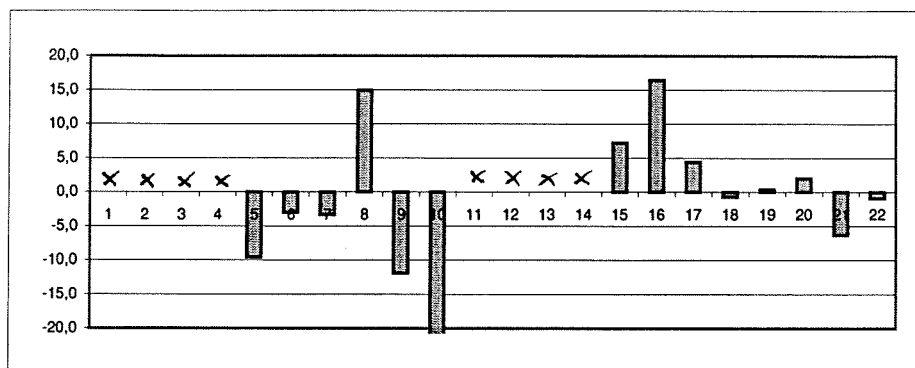
**Chloride, % relative deviation. Laboratory 13**



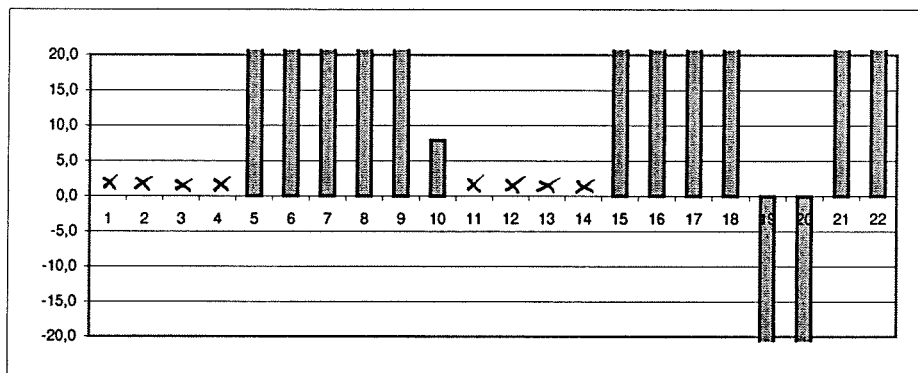
**Chloride, % relative deviation. Laboratory 14**



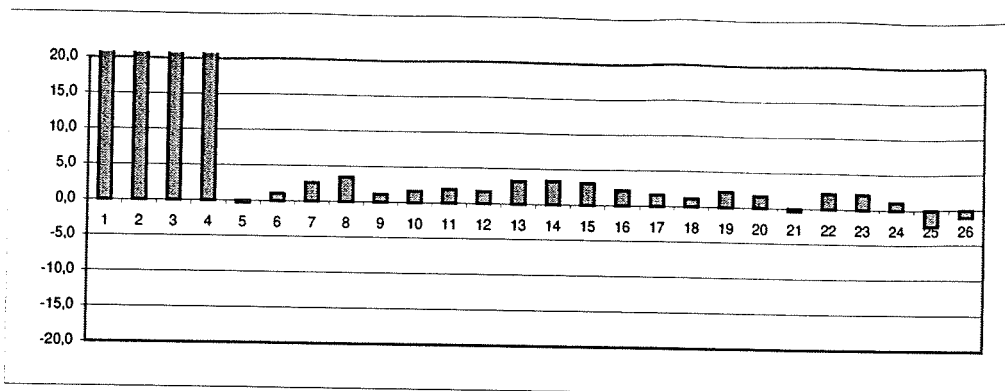
**Chloride, % relative deviation. Laboratory 15**



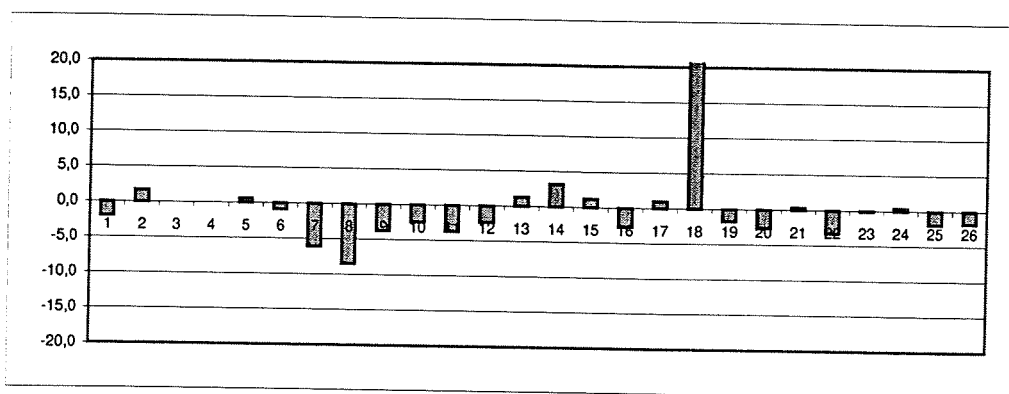
**Chloride, % relative deviation. Laboratory 16**



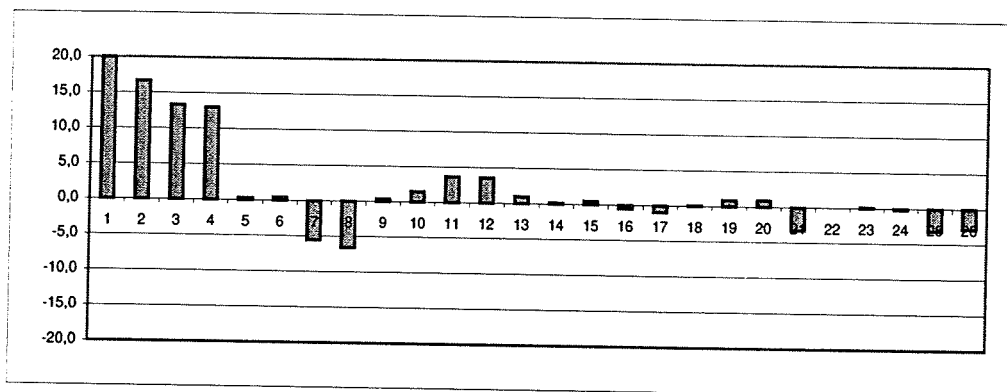
Sulfate, % relative deviation. Laboratory 1



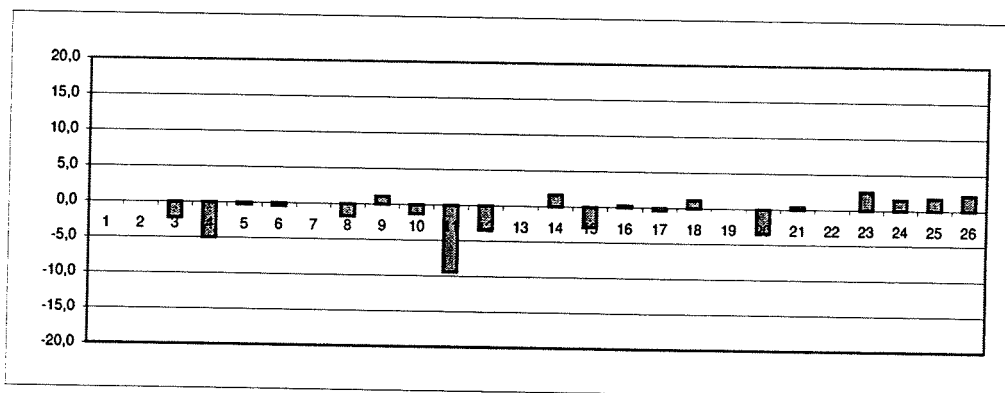
Sulfate, % relative deviation. Laboratory 2



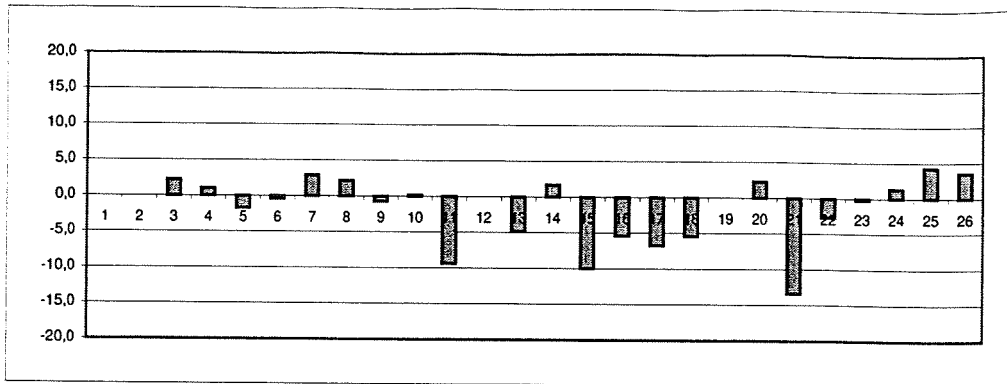
Sulfate, % relative deviation. Laboratory 3



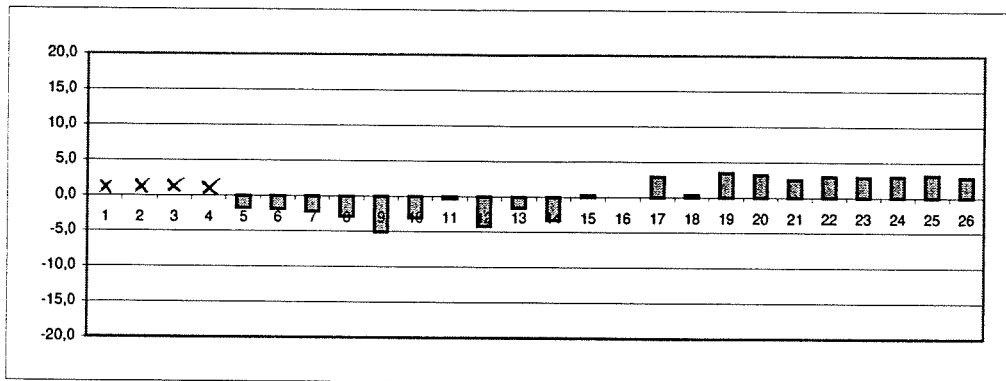
Sulfate, % relative deviation. Laboratory 4



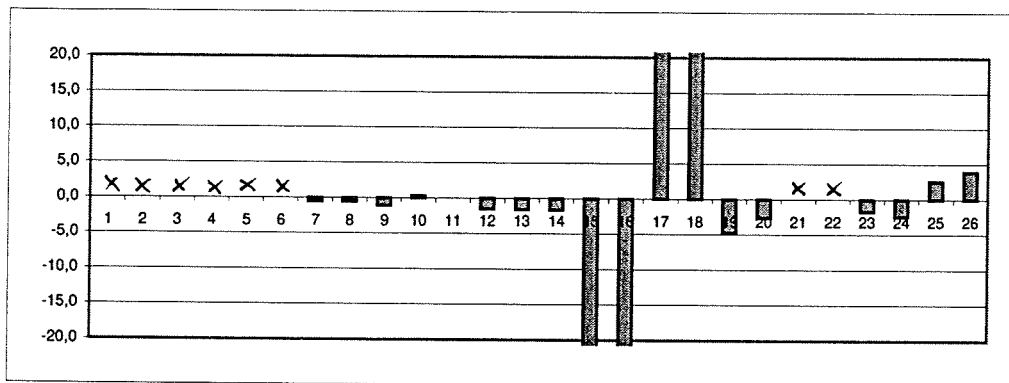
**Sulfate, % relative deviation. Laboratory 5**



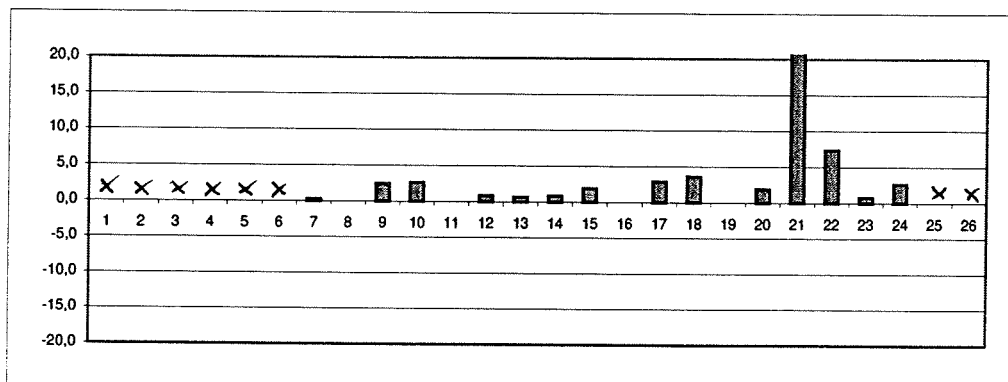
**Sulfate, % relative deviation. Laboratory 6**



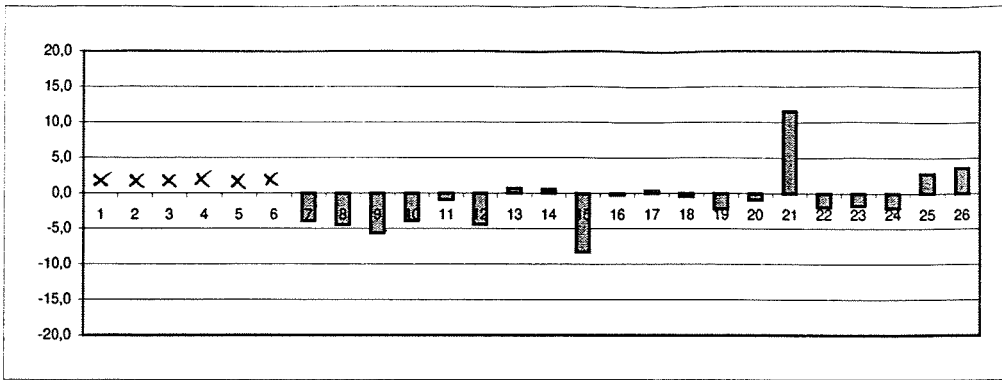
**Sulfate, % relative deviation. Laboratory 7**



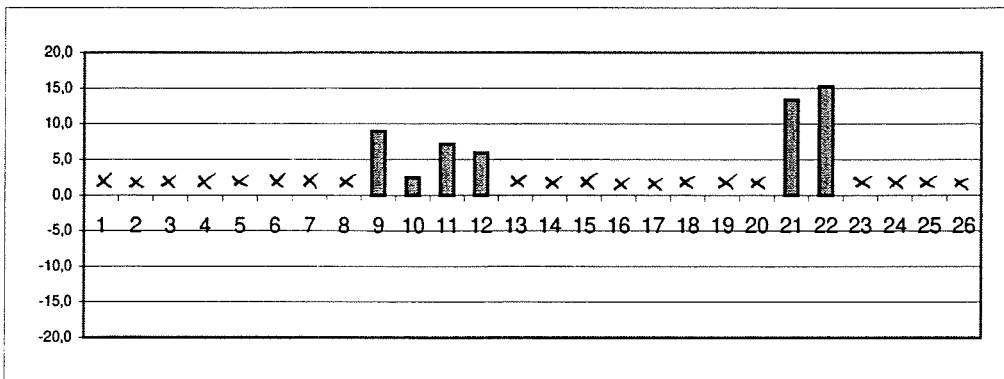
**Sulfate, % relative deviation. Laboratory 8**



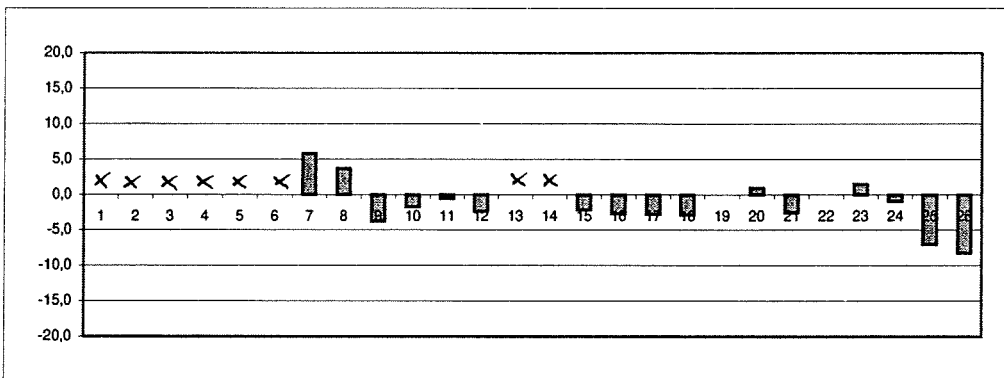
**Sulfate, % relative deviation. Laboratory 9**



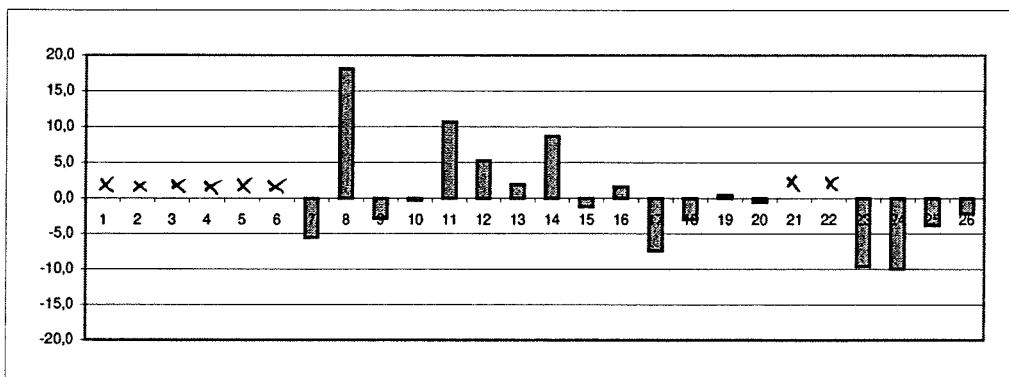
**Sulfate, % relative deviation. Laboratory 10**



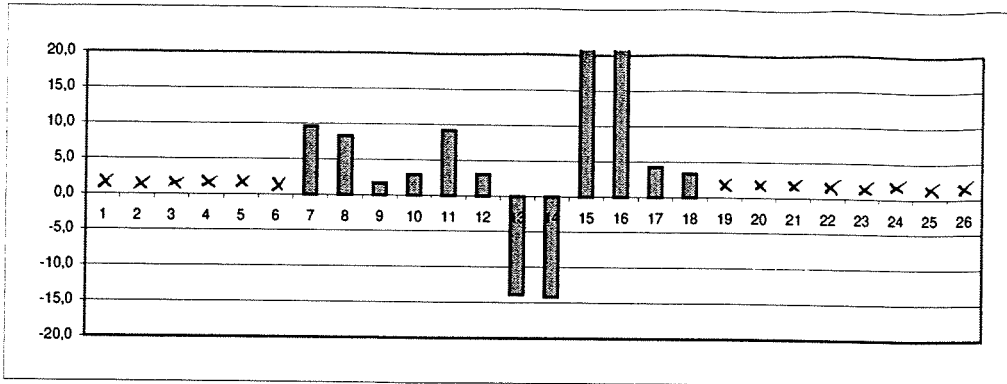
**Sulfate, % relative deviation. Laboratory 11**



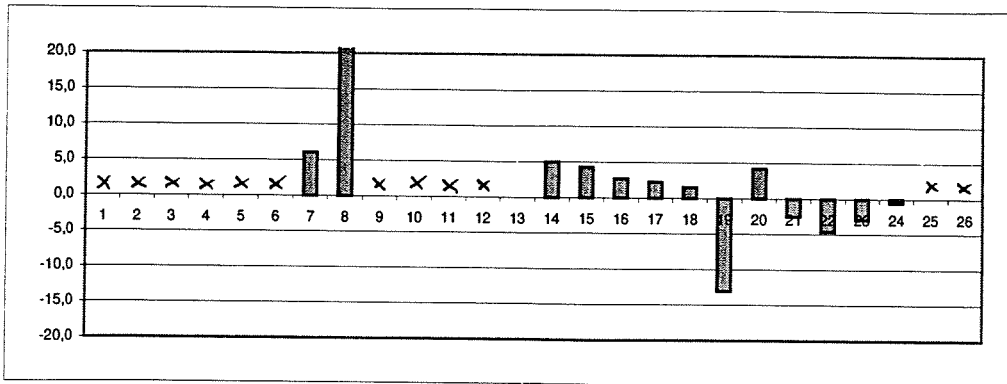
**Sulfate, % relative deviation. Laboratory 12**



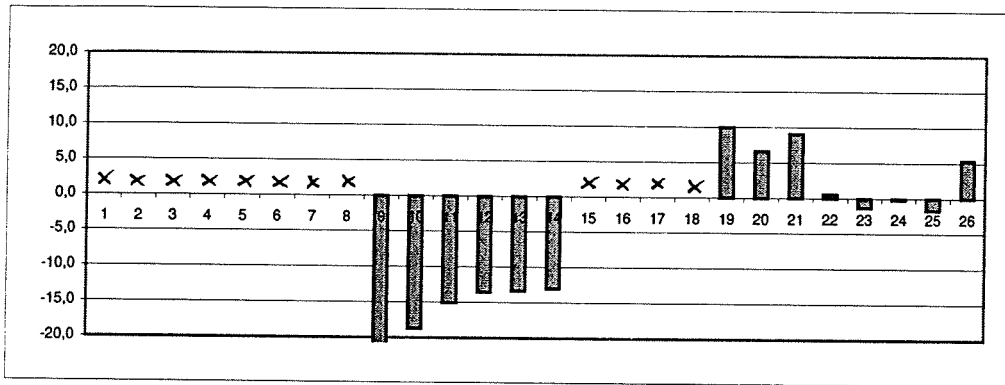
Sulfate, % relative deviation. Laboratory 13



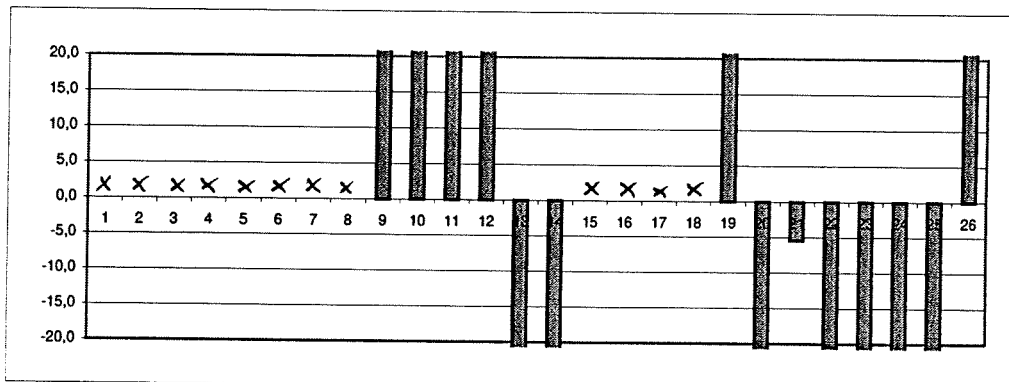
Sulfate, % relative deviation. Laboratory 14



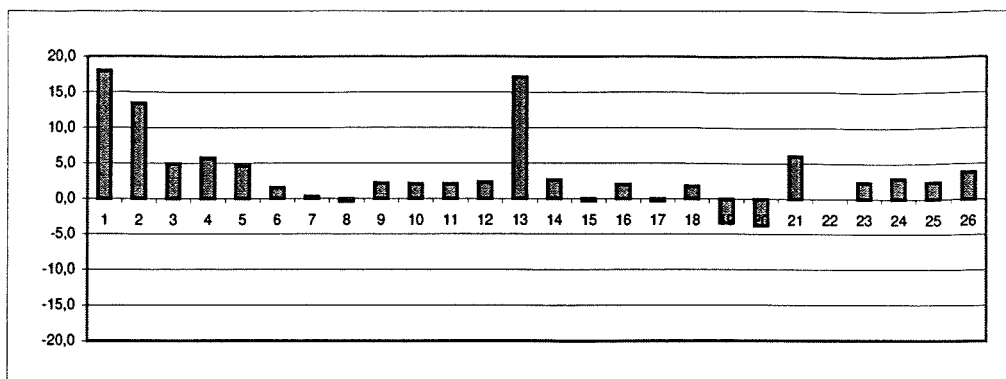
Sulfate, % relative deviation. Laboratory 15



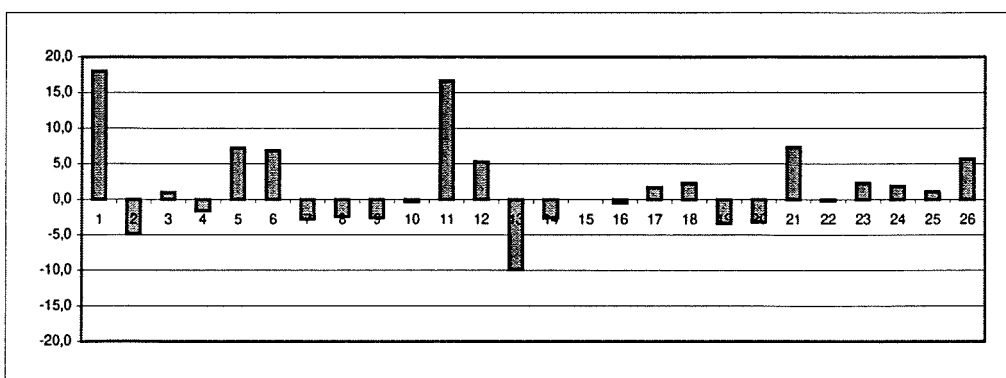
Sulfate, % relative deviation. Laboratory 16



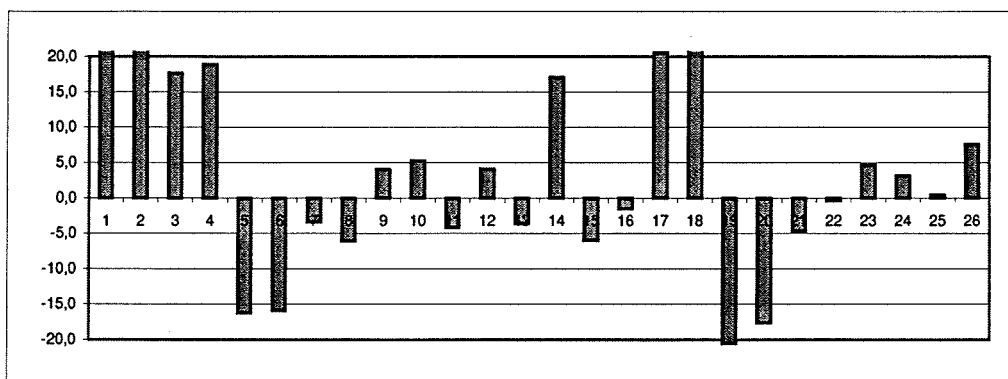
**Calcium % relative deviation. Laboratory 1**



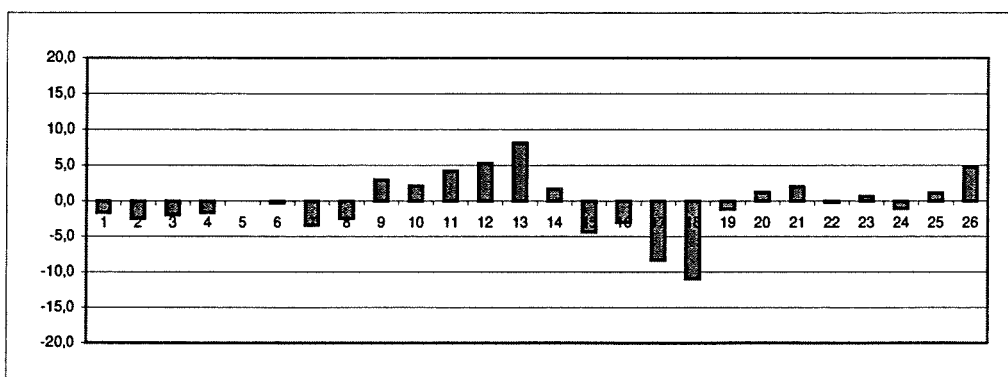
**Calcium % relative deviation. Laboratory 2**



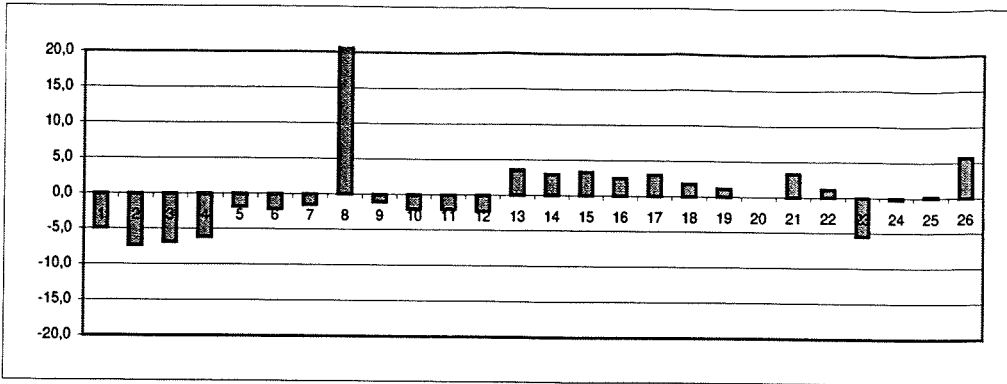
**Calcium % relative deviation. Laboratory 3**



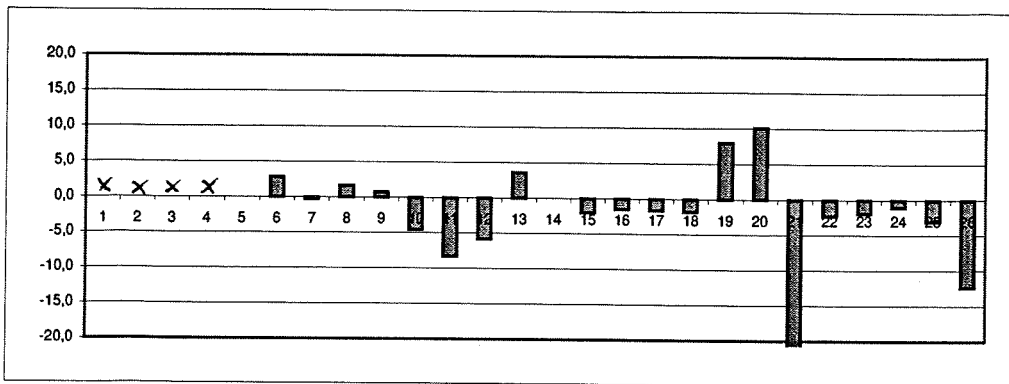
**Calcium % relative deviation. Laboratory 4**



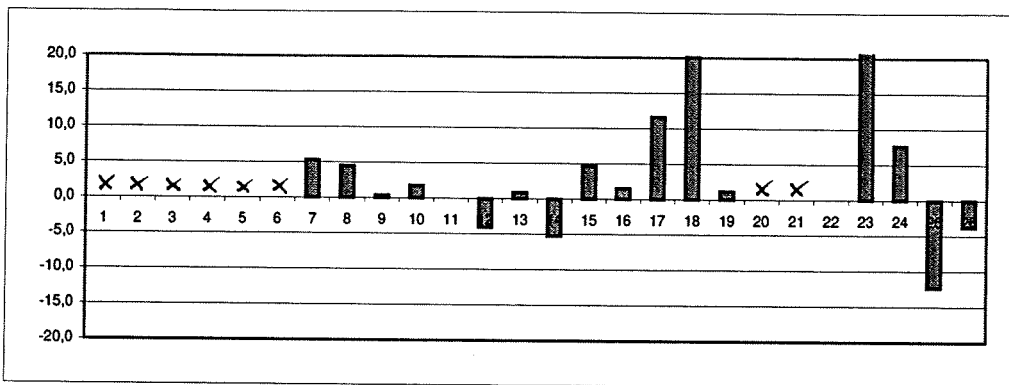
**Calcium % relative deviation. Laboratory 5**



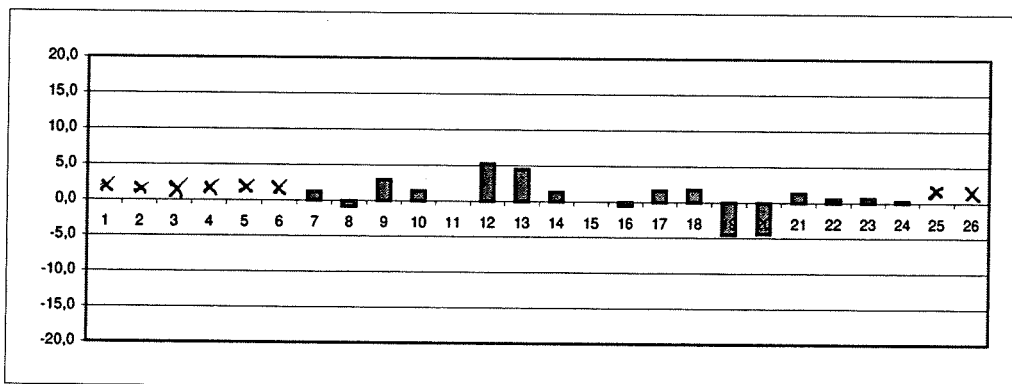
**Calcium % relative deviation. Laboratory 6**



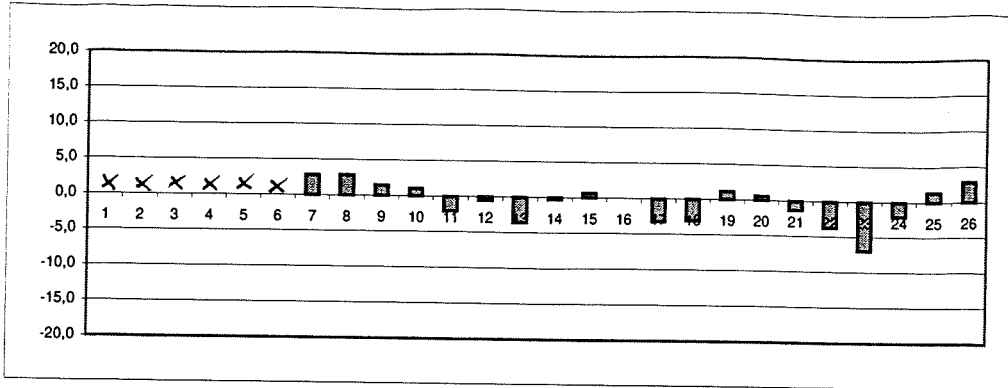
**Calcium % relative deviation. Laboratory 7**



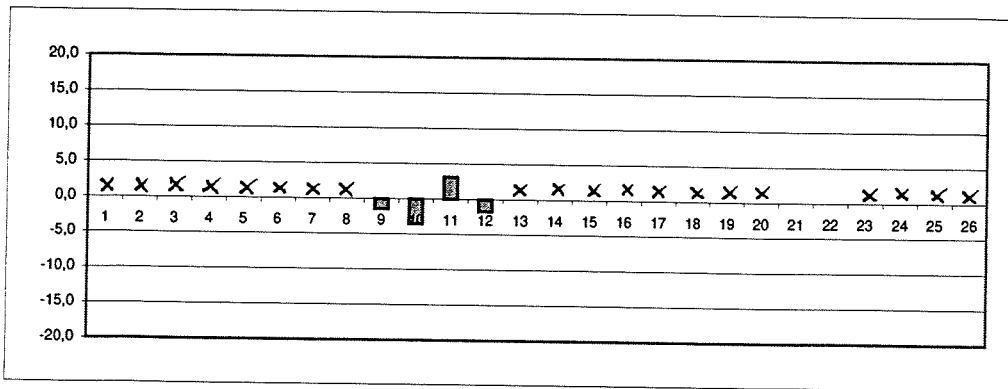
**Calcium % relative deviation. Laboratory 8**



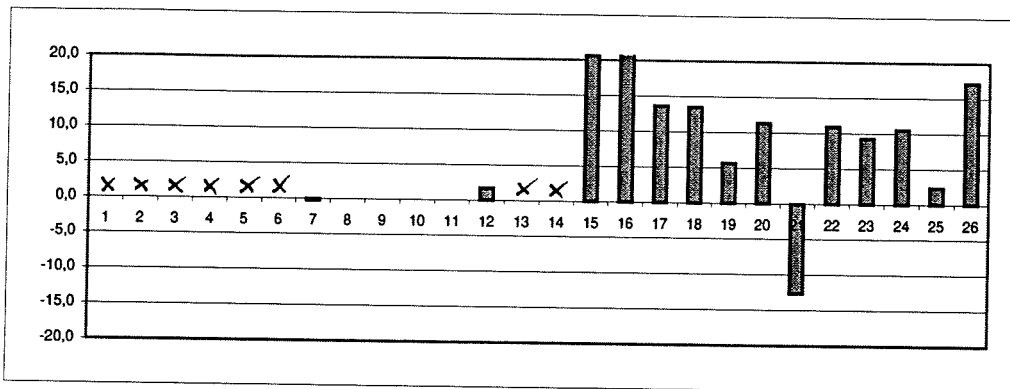
**Calcium % relative deviation. Laboratory 9**



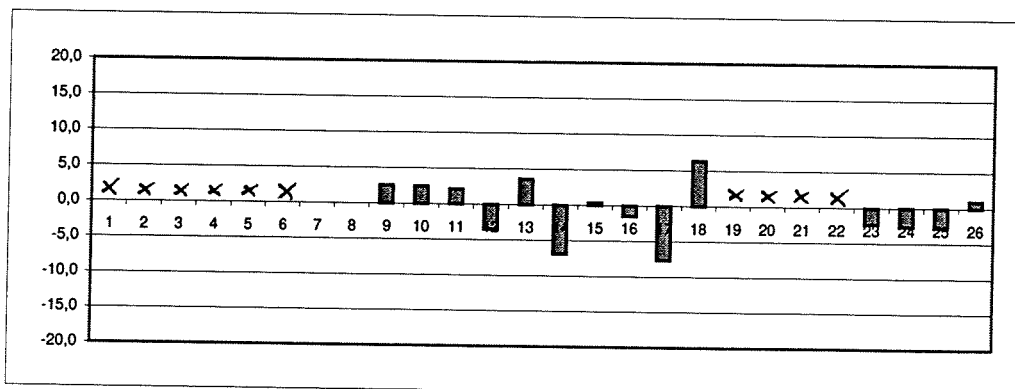
**Calcium % relative deviation. Laboratory 10**



**Calcium % relative deviation. Laboratory 11**

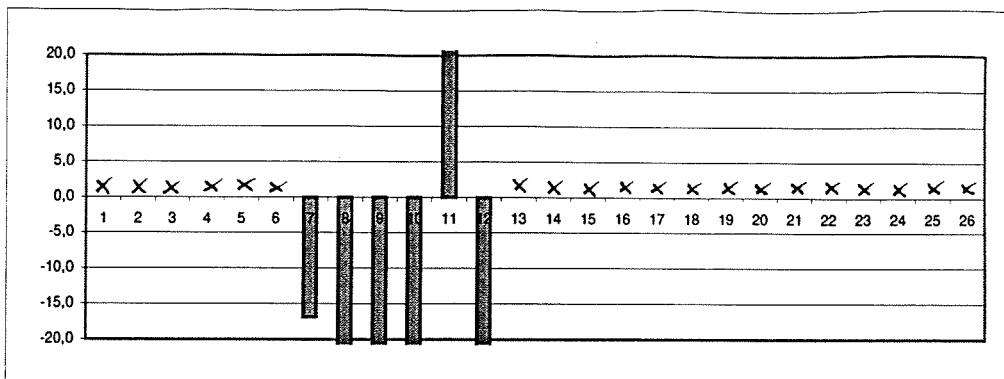


**Calcium % relative deviation. Laboratory 12**

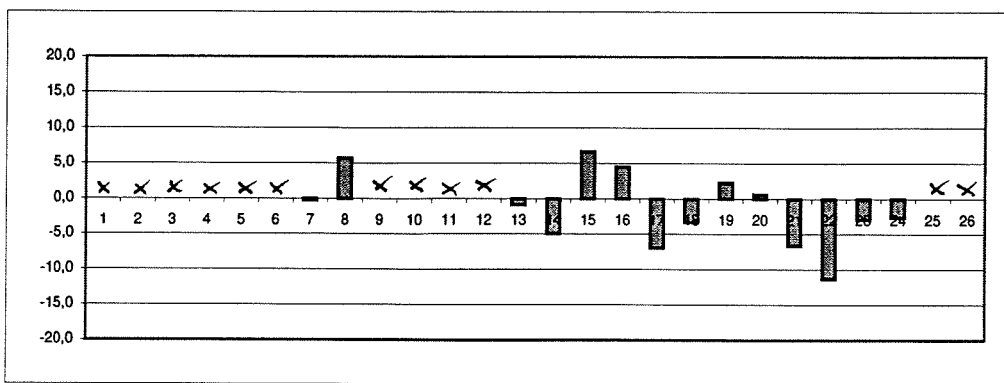




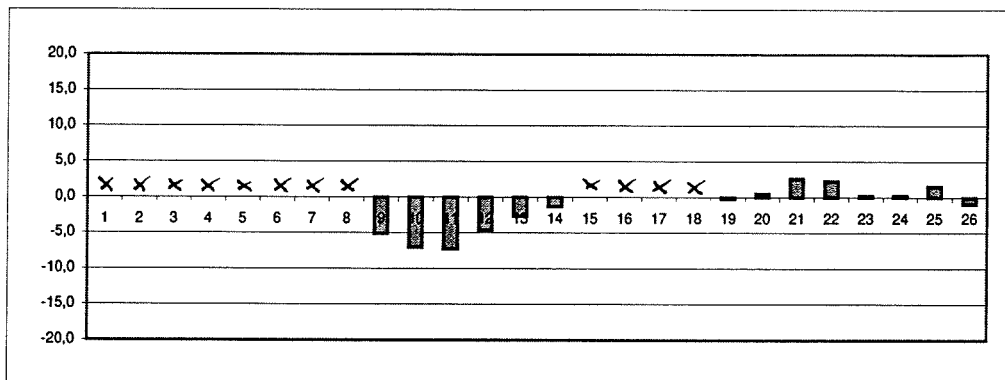
**Calcium % relative deviation. Laboratory 13**



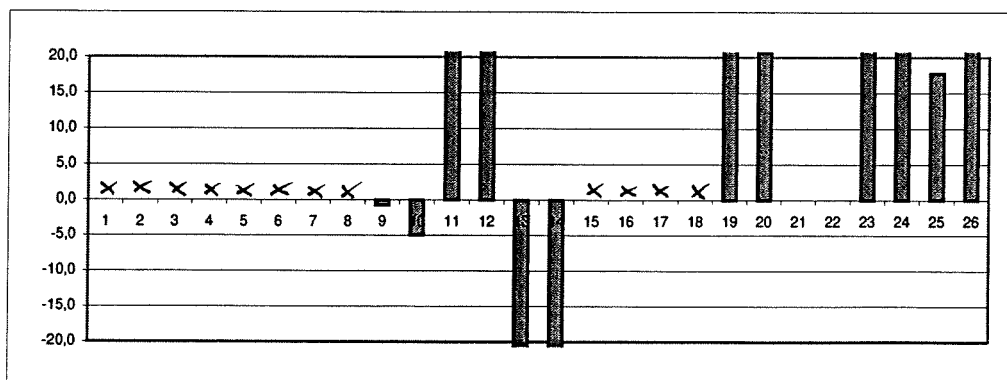
**Calcium % relative deviation. Laboratory 14**



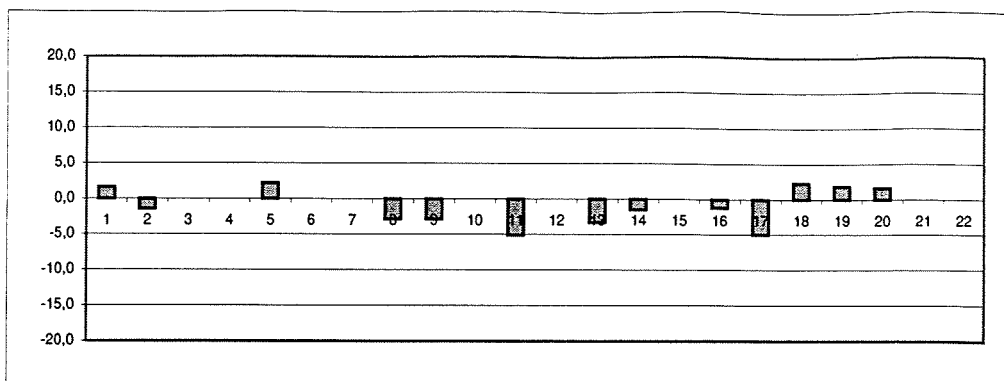
**Calcium % relative deviation. Laboratory 15**



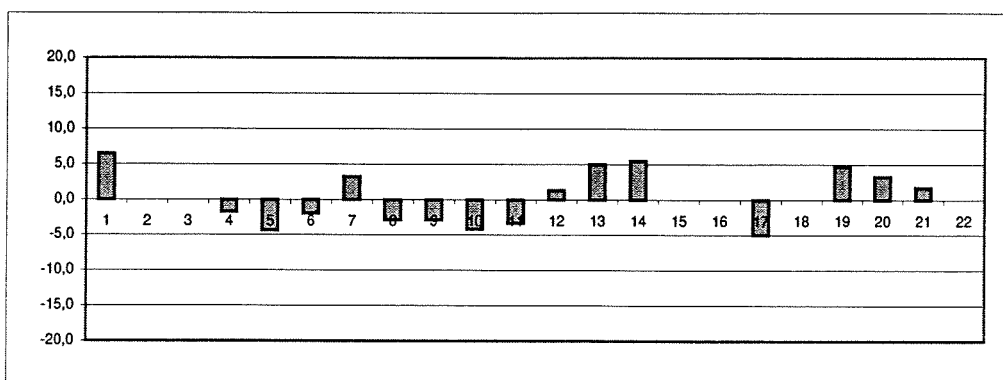
**Calcium % relative deviation. Laboratory 16**



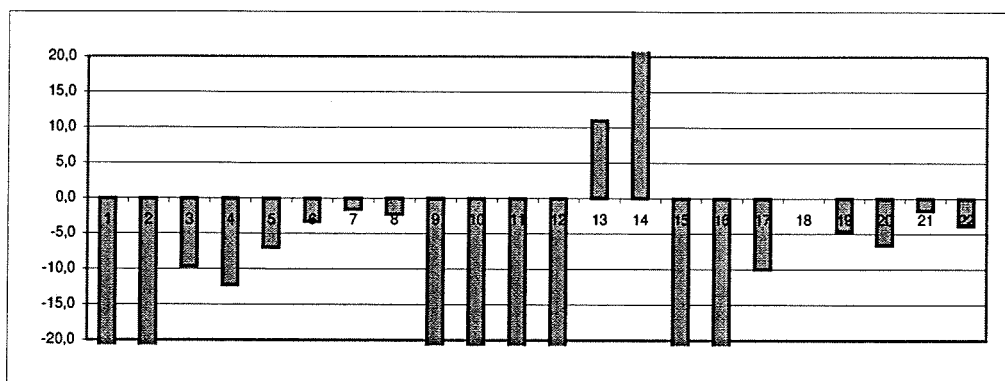
**Magnesium, % relative deviation. Laboratory 1**



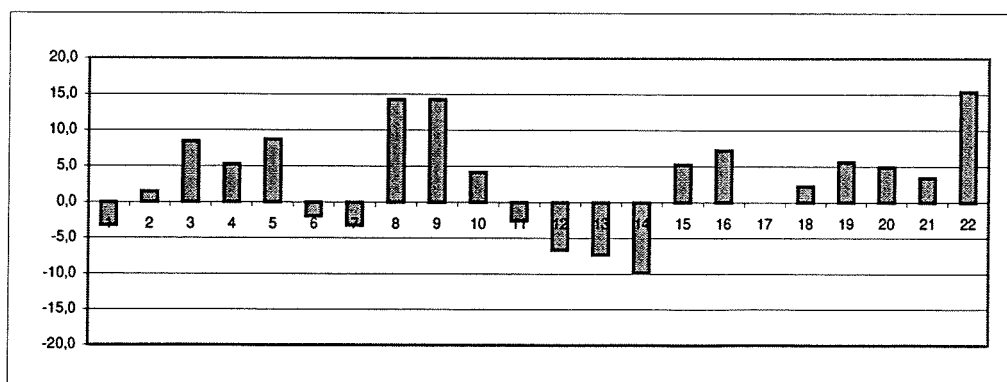
**Magnesium, % relative deviation. Laboratory 2**



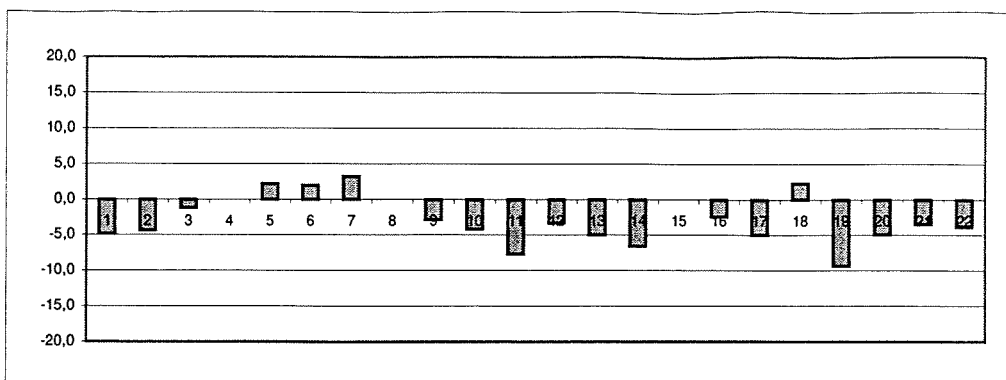
**Magnesium, % relative deviation. Laboratory 3**



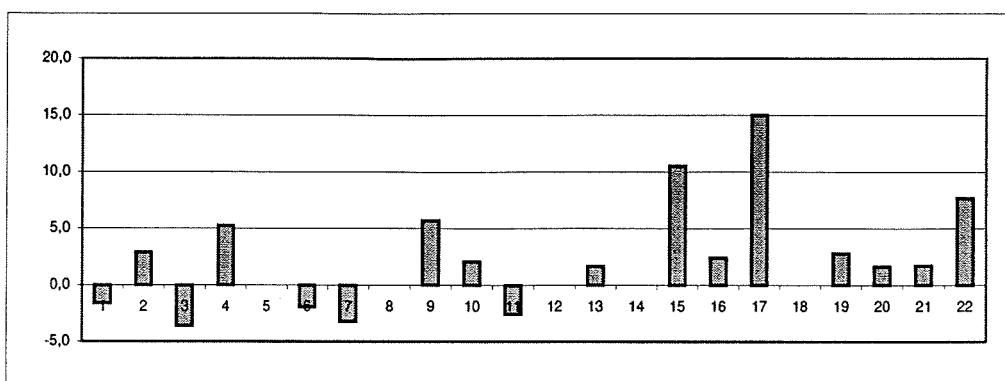
**Magnesium, % relative deviation. Laboratory 4**



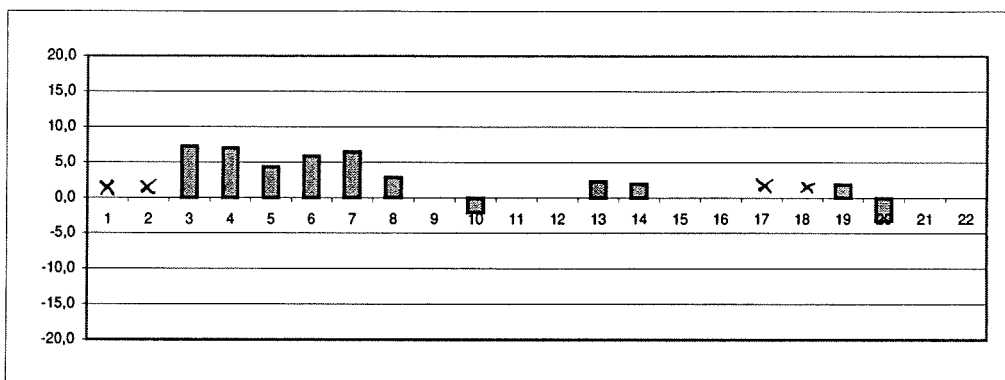
**Magnesium, % relative deviation. Laboratory 5**



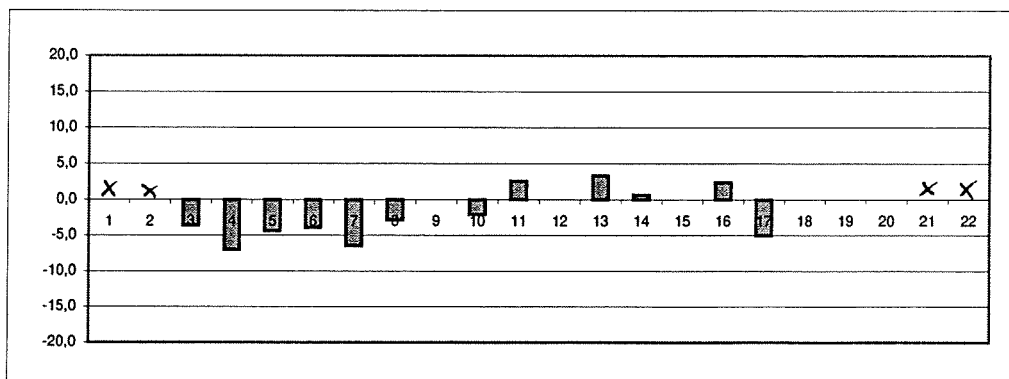
**Magnesium, % relative deviation. Laboratory 6**



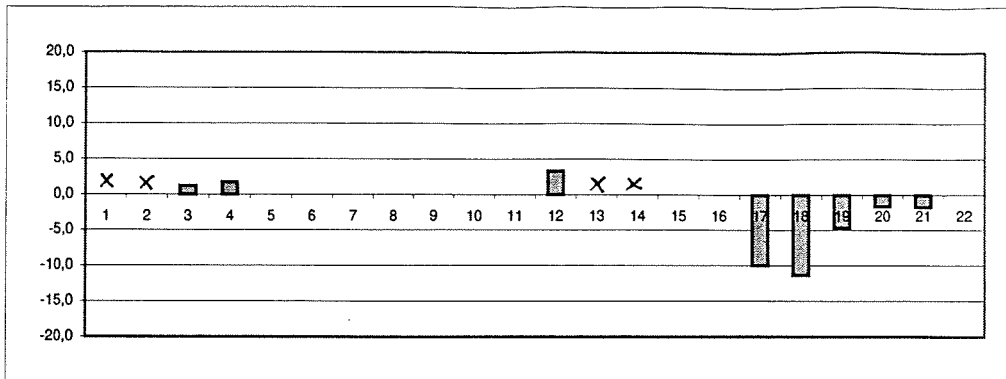
**Magnesium, % relative deviation. Laboratory 7**



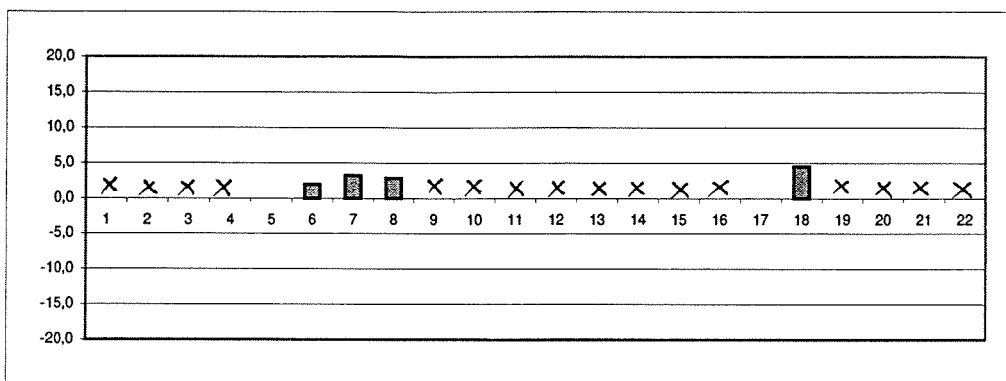
**Magnesium, % relative deviation. Laboratory 8**



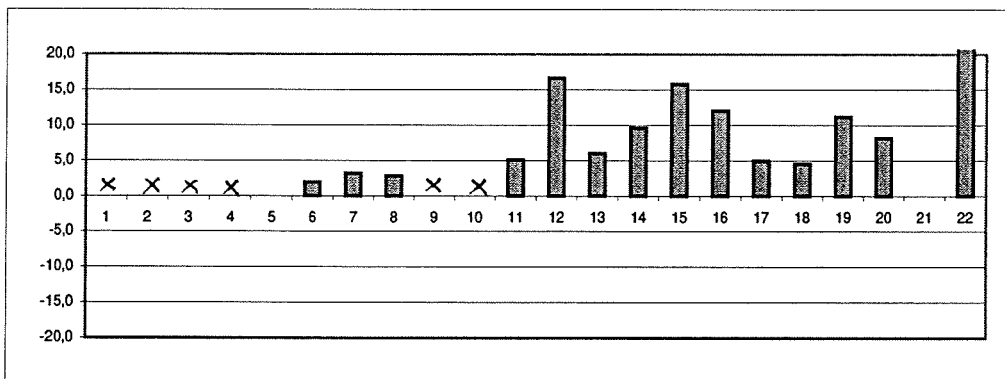
**Magnesium, % relative deviation. Laboratory 9**



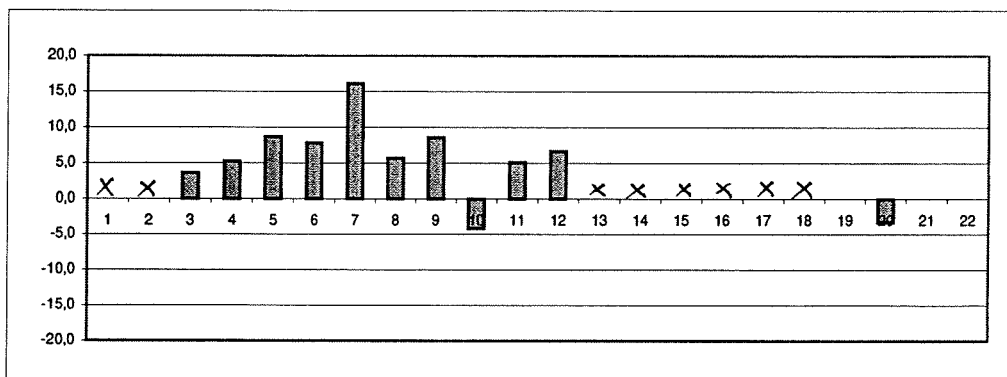
**Magnesium, % relative deviation. Laboratory 10**



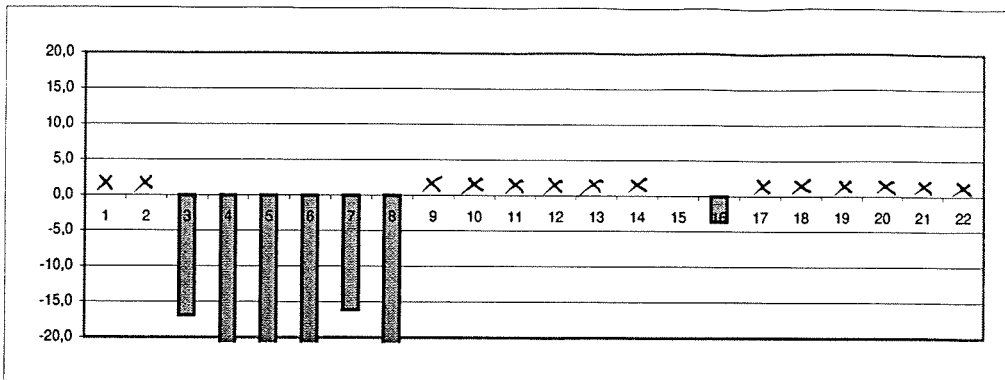
**Magnesium, % relative deviation. Laboratory 11**



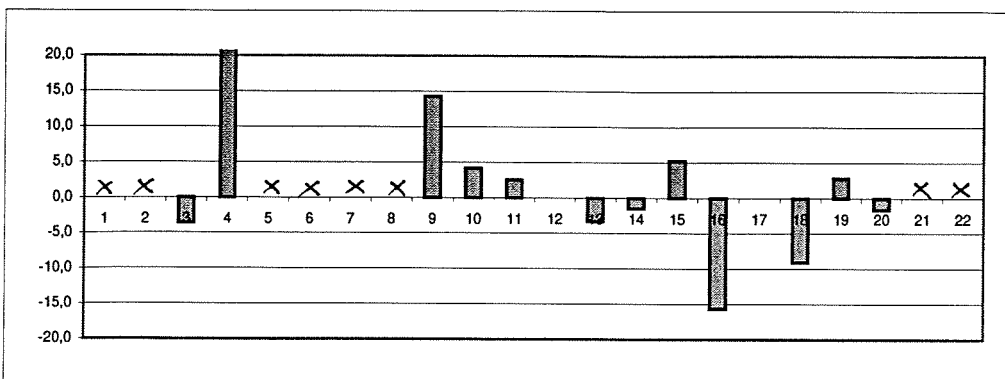
**Magnesium, % relative deviation. Laboratory 12**



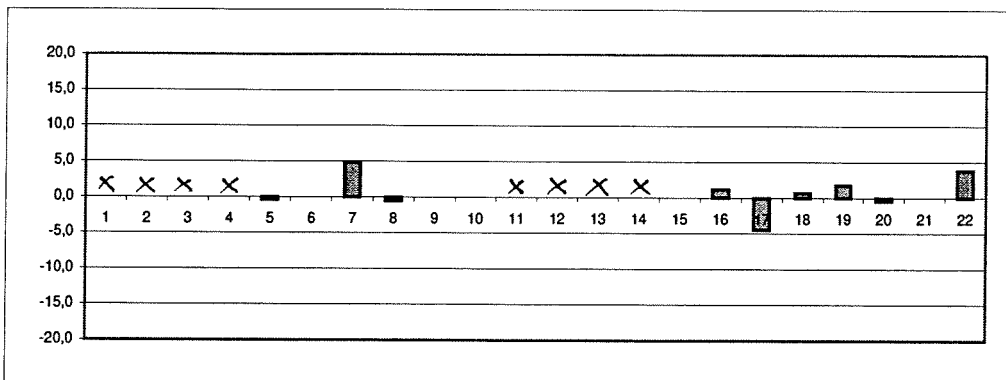
**Magnesium, % relative deviation. Laboratory 13**



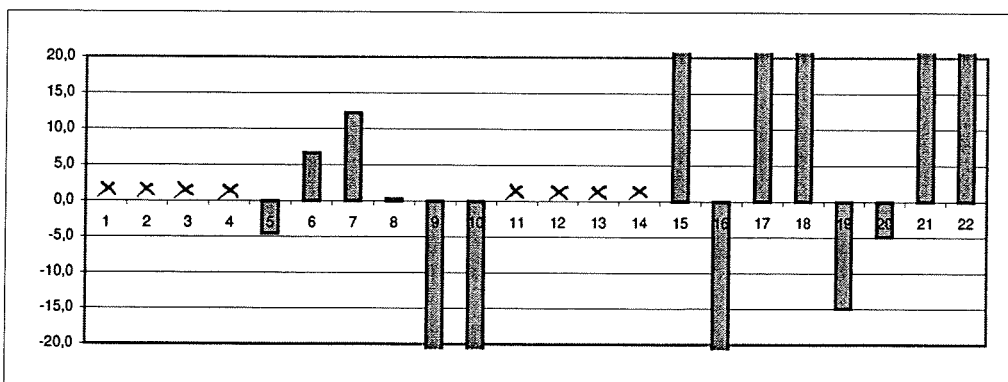
**Magnesium, % relative deviation. Laboratory 14**



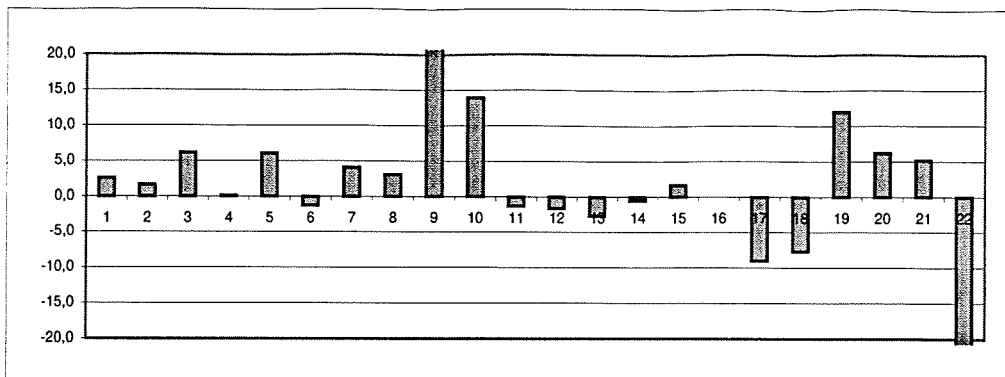
**Magnesium, % relative deviation. Laboratory 15**



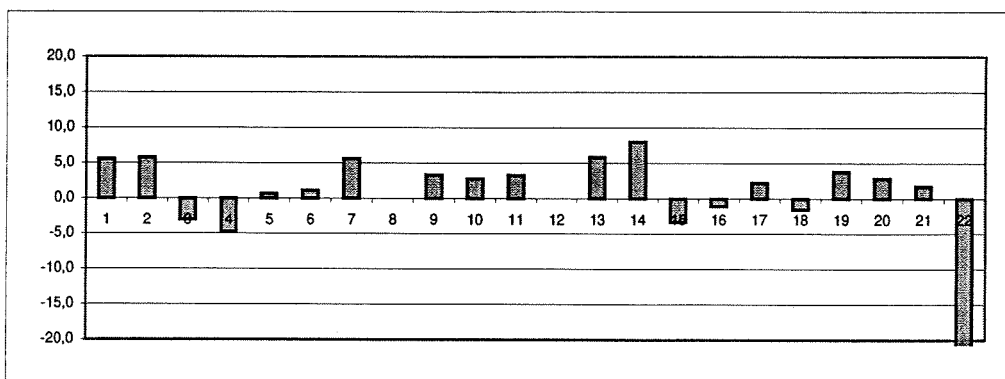
**Magnesium, % relative deviation. Laboratory 16**



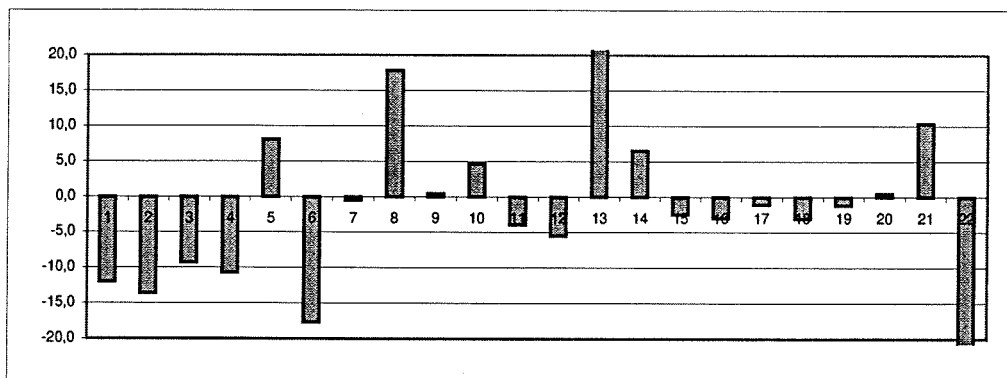
**Sodium, % relative deviation. Laboratory 1**



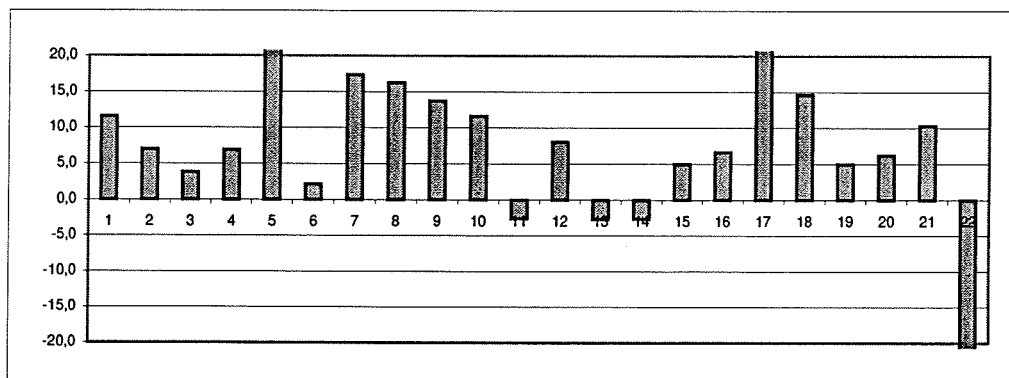
**Sodium, % relative deviation. Laboratory 2**



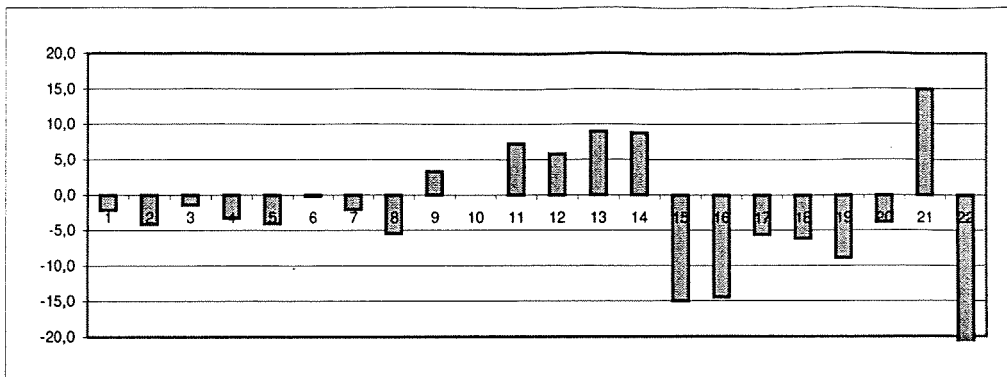
**Sodium, % relative deviation. Laboratory 3**



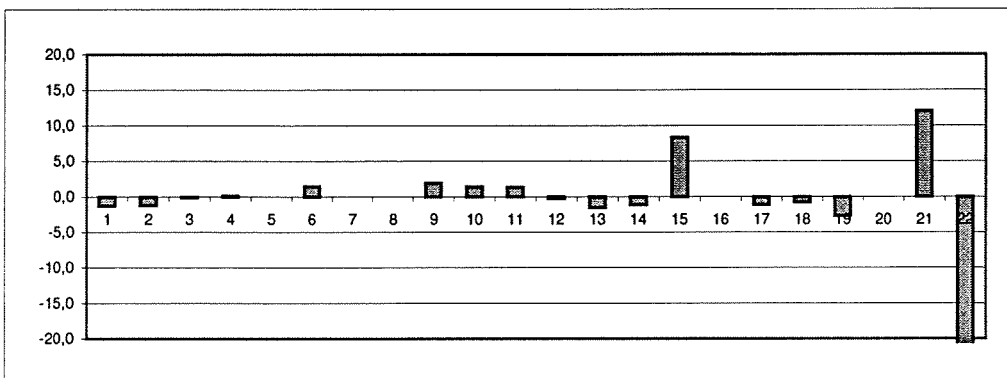
**Sodium, % relative deviation. Laboratory 4**



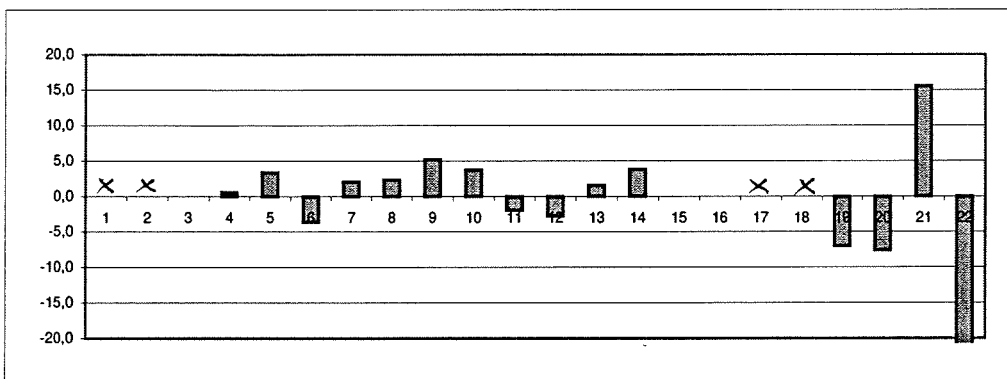
Sodium, % relative deviation. Laboratory 5



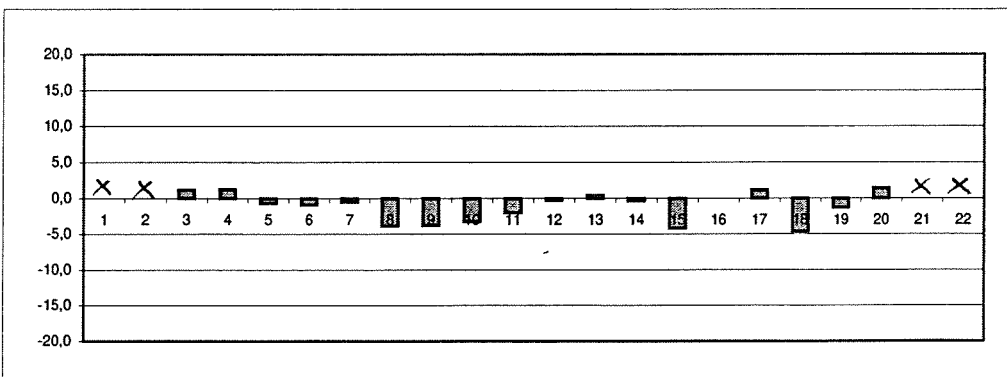
Sodium, % relative deviation. Laboratory 6



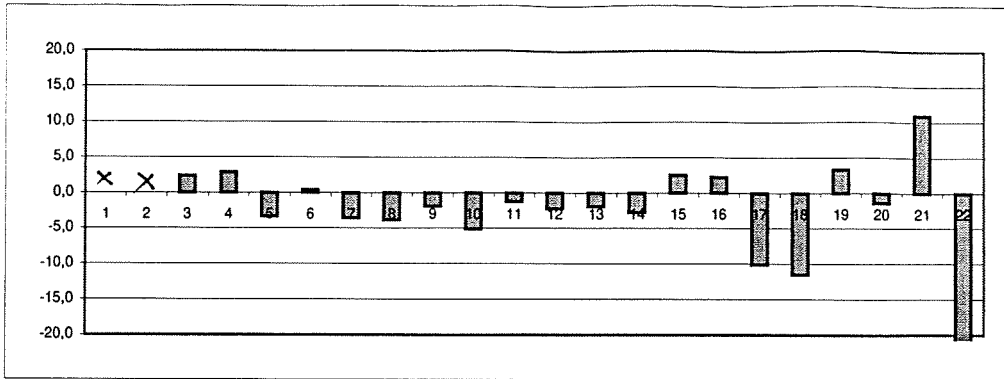
Sodium, % relative deviation. Laboratory 7



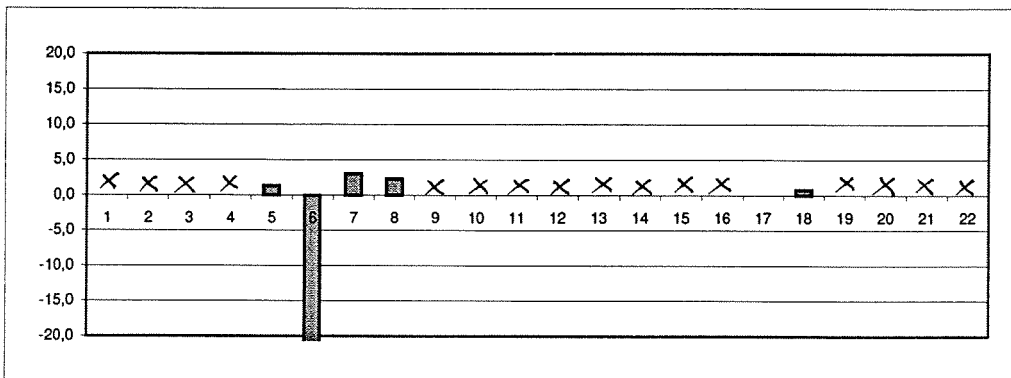
Sodium, % relative deviation. Laboratory 8



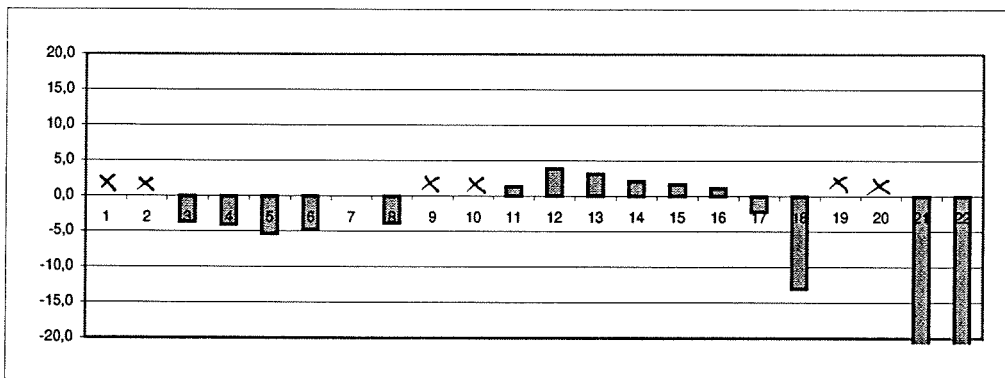
**Sodium, % relative deviation. Laboratory 9**



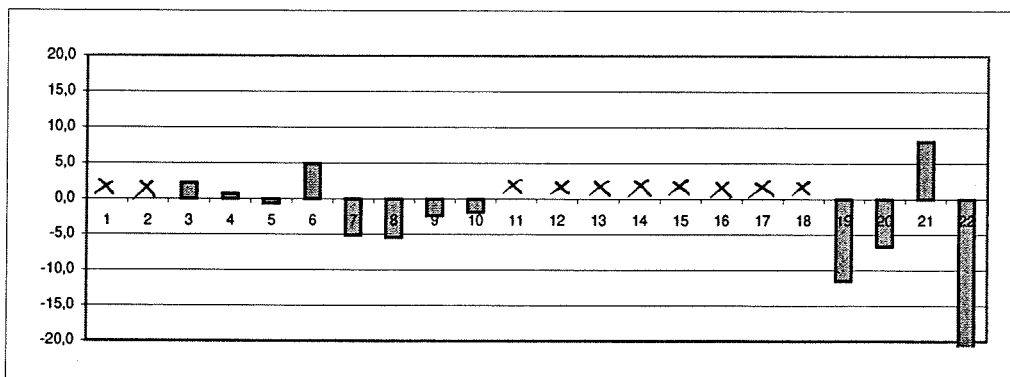
**Sodium, % relative deviation. Laboratory 10**



**Sodium, % relative deviation. Laboratory 11**

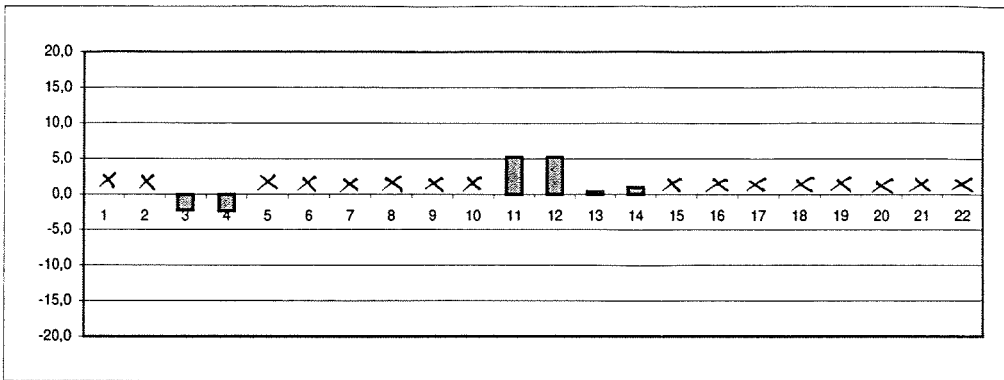


**Sodium, % relative deviation. Laboratory 12**

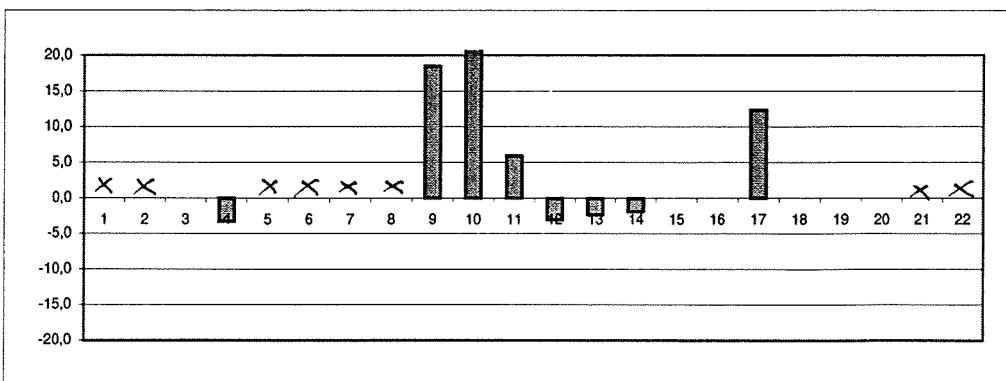




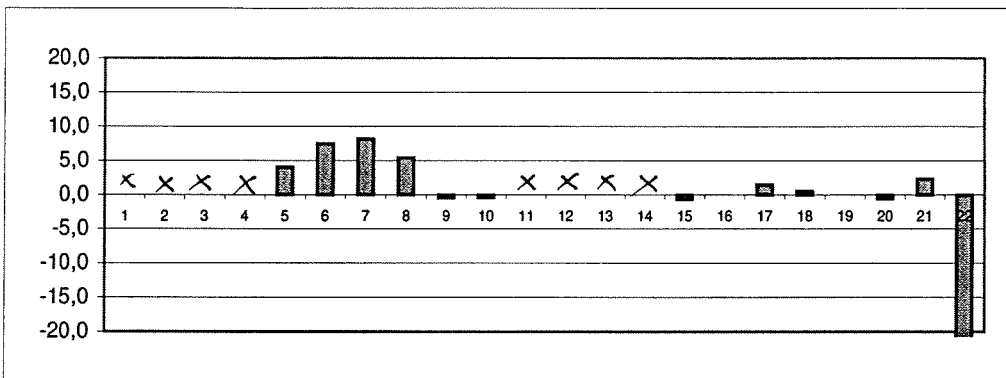
Sodium, % relative deviation. Laboratory 13



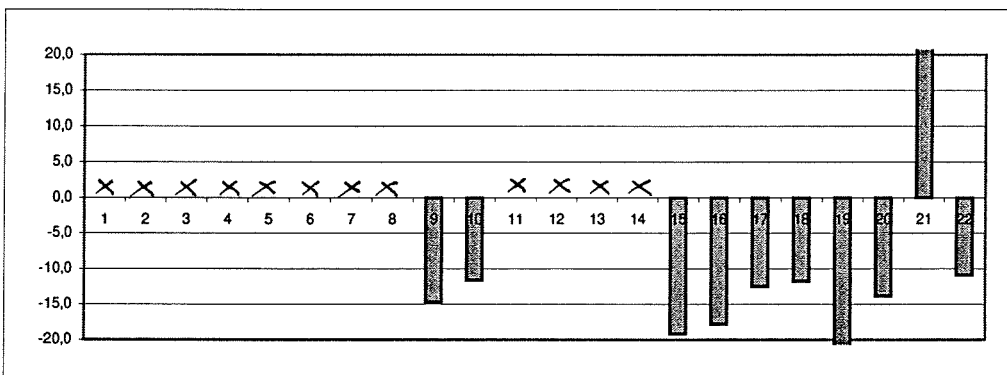
Sodium, % relative deviation. Laboratory 14



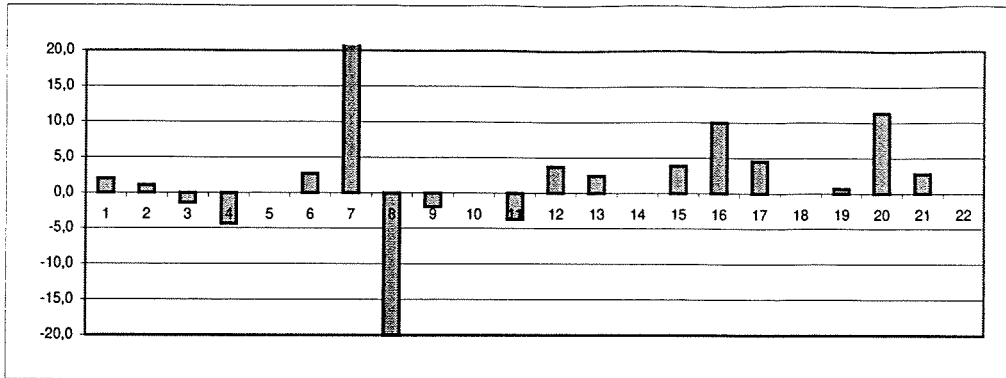
Sodium, % relative deviation. Laboratory 15



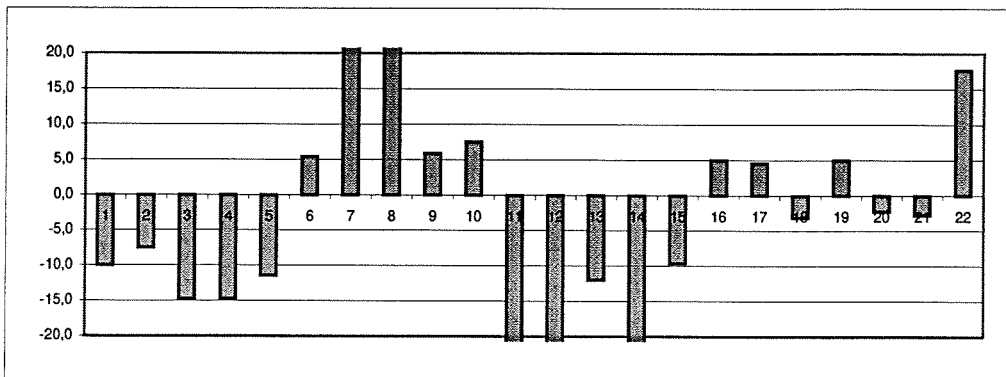
Sodium, % relative deviation. Laboratory 16



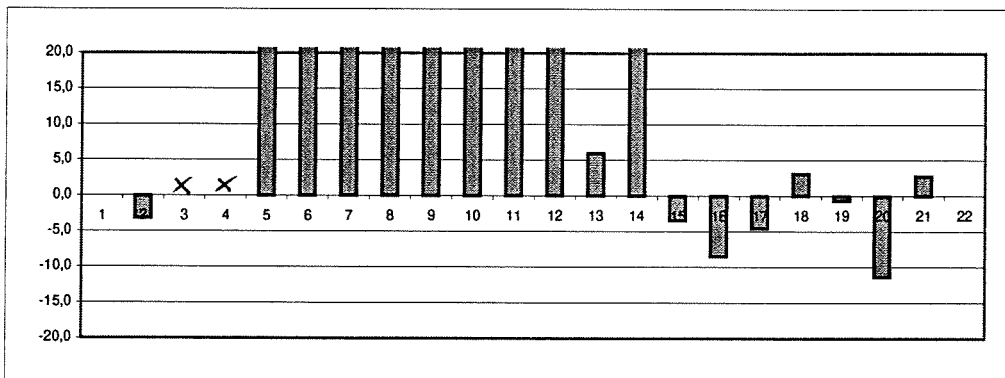
**Potassium, % relative deviation. Laboratory 1**



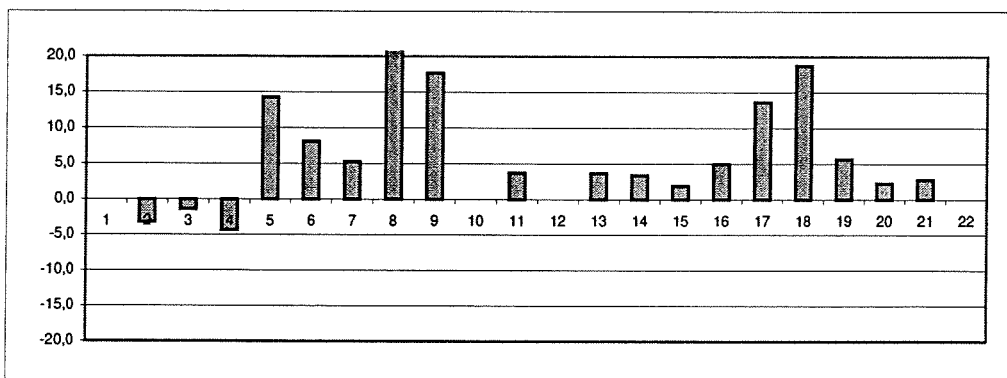
**Potassium, % relative deviation. Laboratory 2**



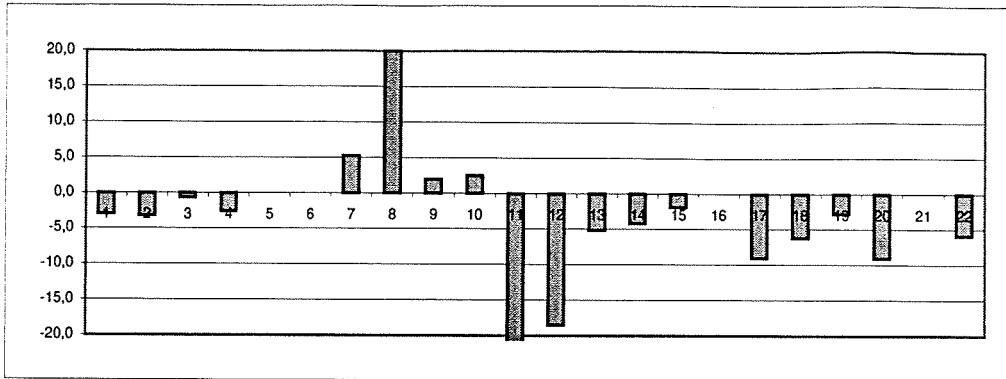
**Potassium, % relative deviation. Laboratory 3**



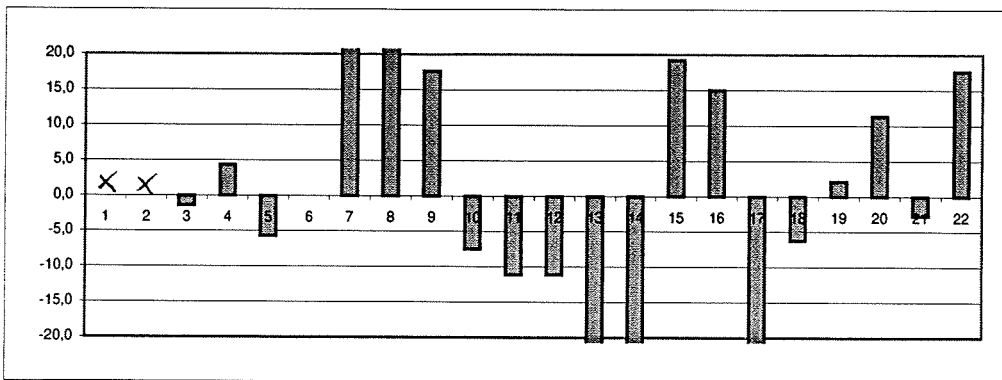
**Potassium, % relative deviation. Laboratory 4**



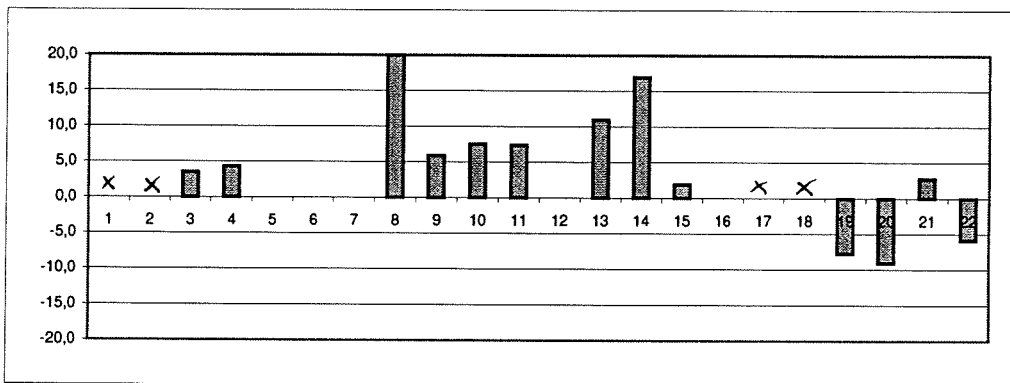
**Potassium, % relative deviation. Laboratory 5**



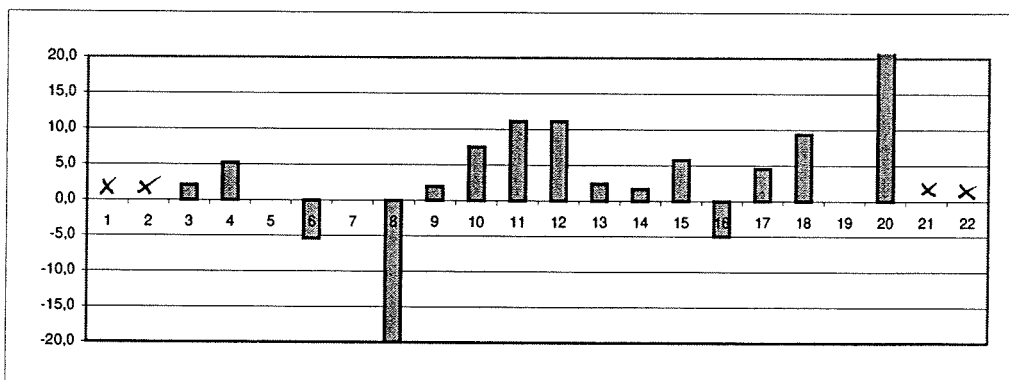
**Potassium, % relative deviation. Laboratory 6**



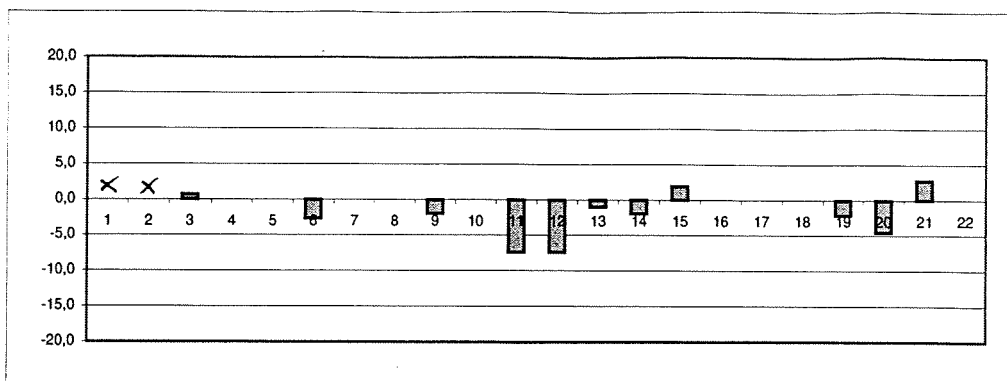
**Potassium, % relative deviation. Laboratory 7**



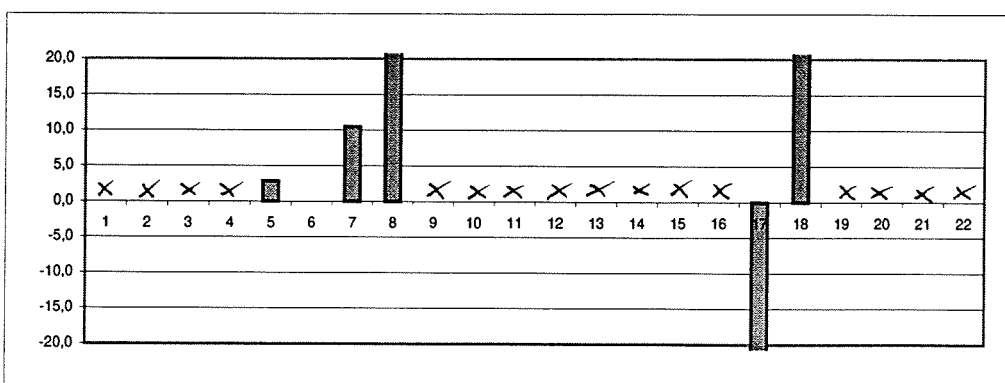
**Potassium, % relative deviation. Laboratory 8**



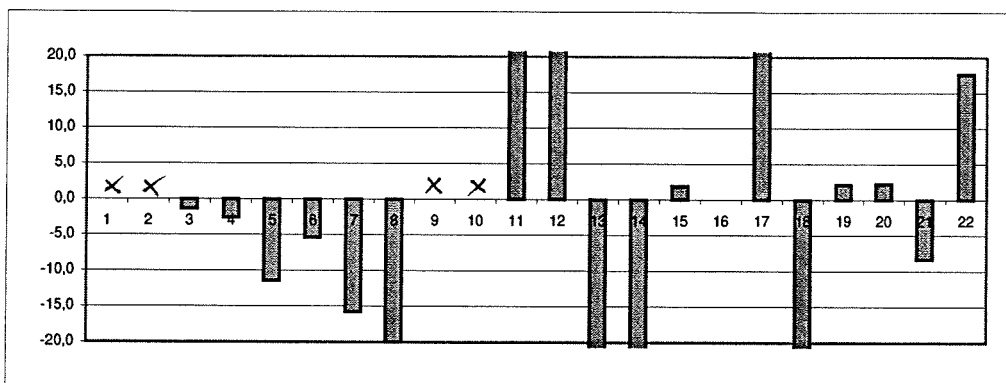
**Potassium, % relative deviation. Laboratory 9**



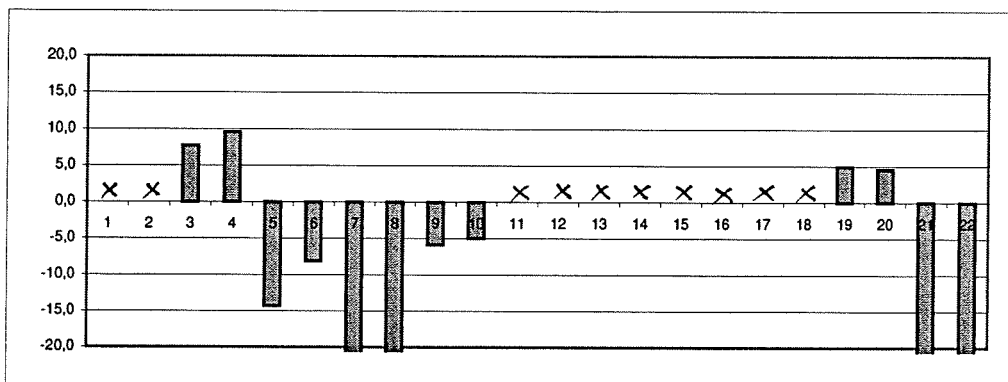
**Potassium, % relative deviation. Laboratory 10**



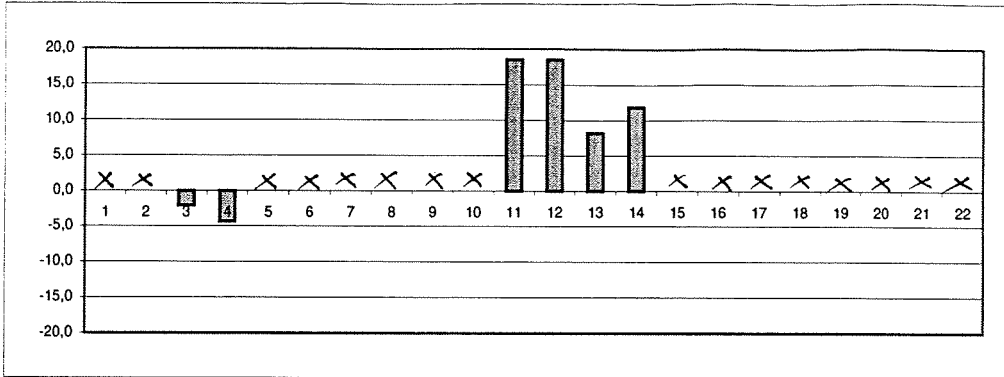
**Potassium, % relative deviation. Laboratory 11**



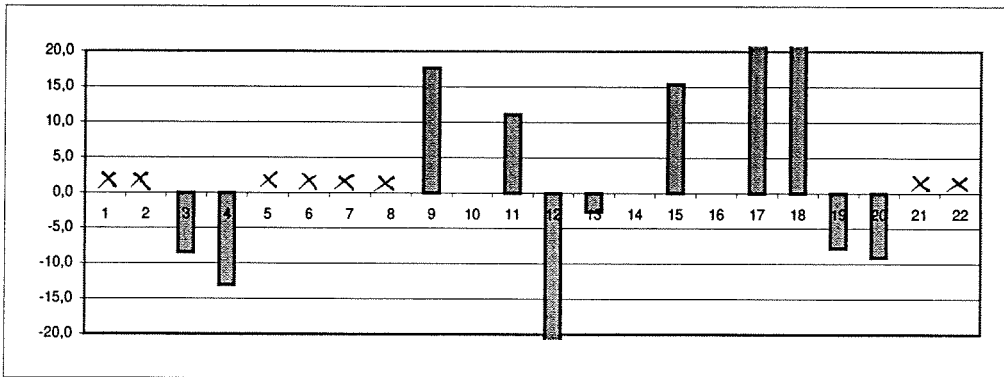
**Potassium, % relative deviation. Laboratory 12**



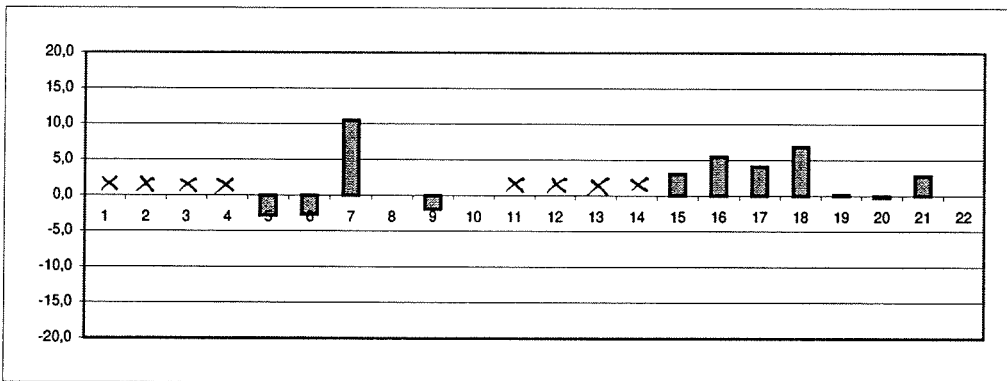
**Potassium, % relative deviation. Laboratory 13**



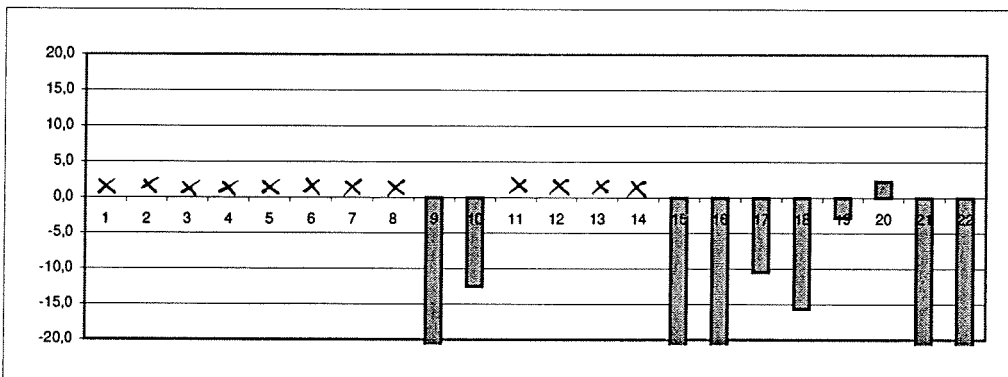
**Potassium, % relative deviation. Laboratory 14**



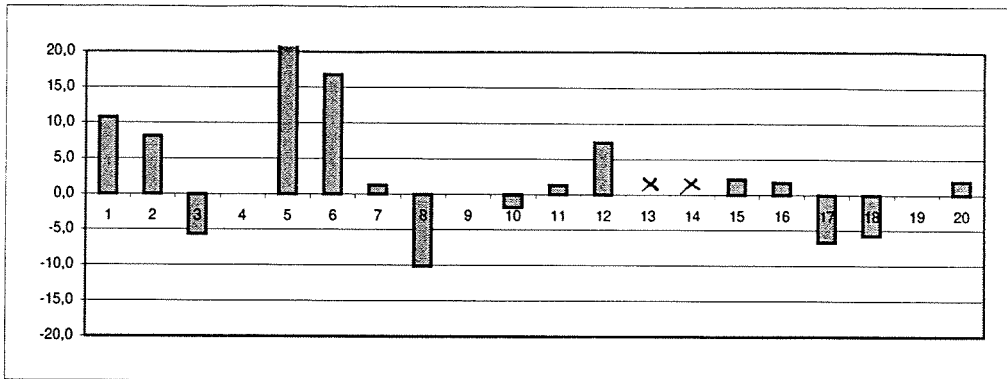
**Potassium, % relative deviation. Laboratory 15**



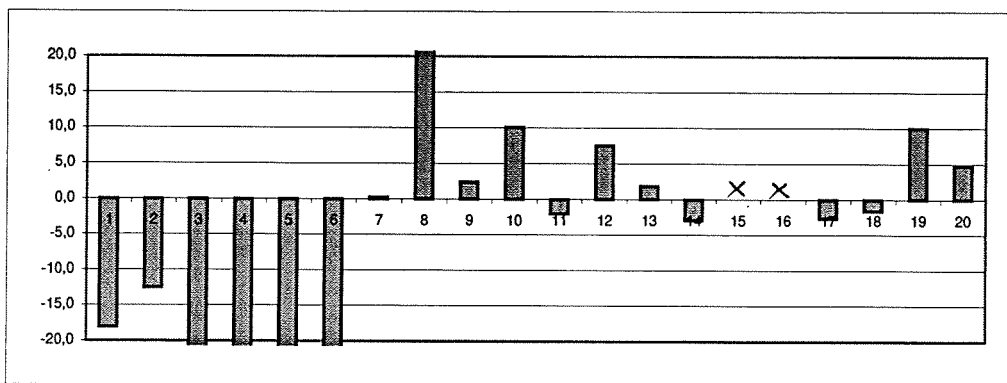
**Potassium, % relative deviation. Laboratory 16**



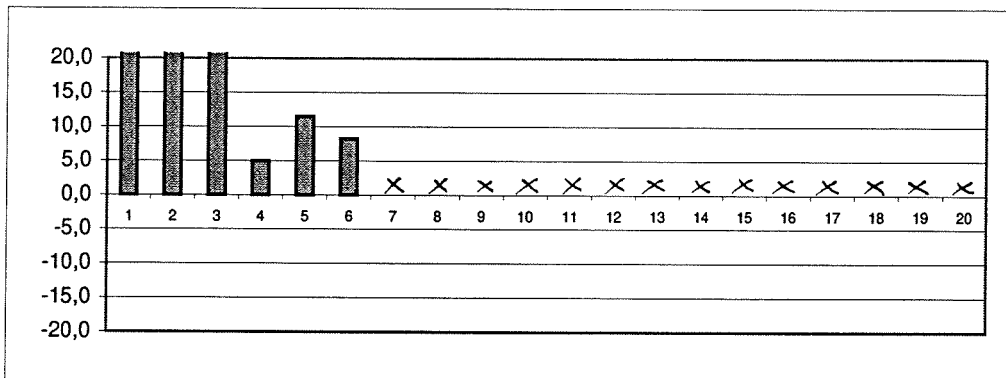
**Aluminium, % relative deviation. Laboratory 1**



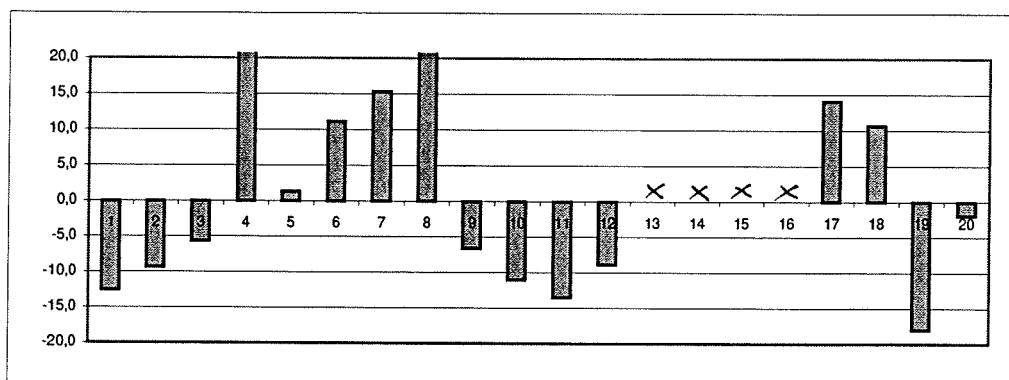
**Aluminium, % relative deviation. Laboratory 2**



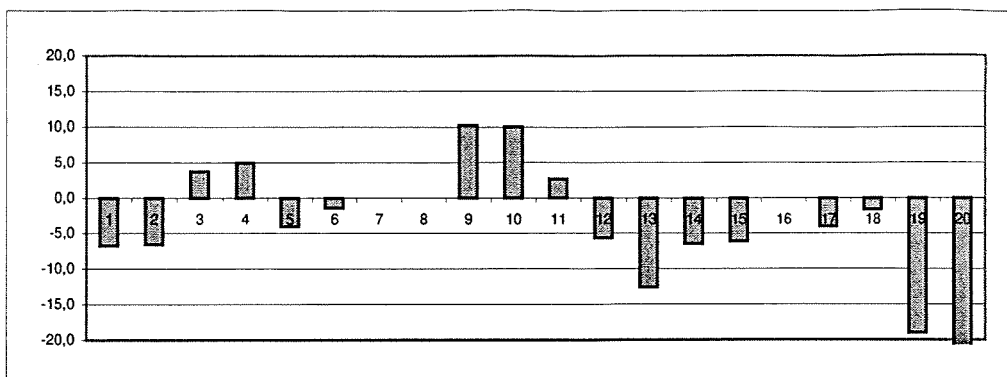
**Aluminium, % relative deviation. Laboratory 3**



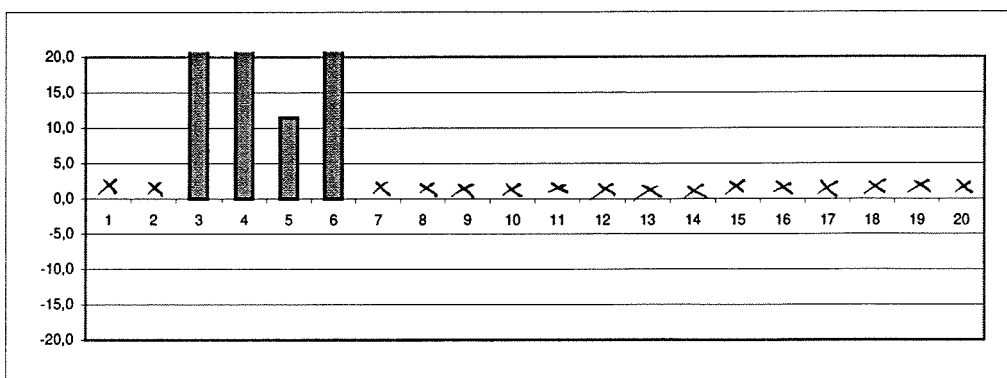
**Aluminium, % relative deviation. Laboratory 4**



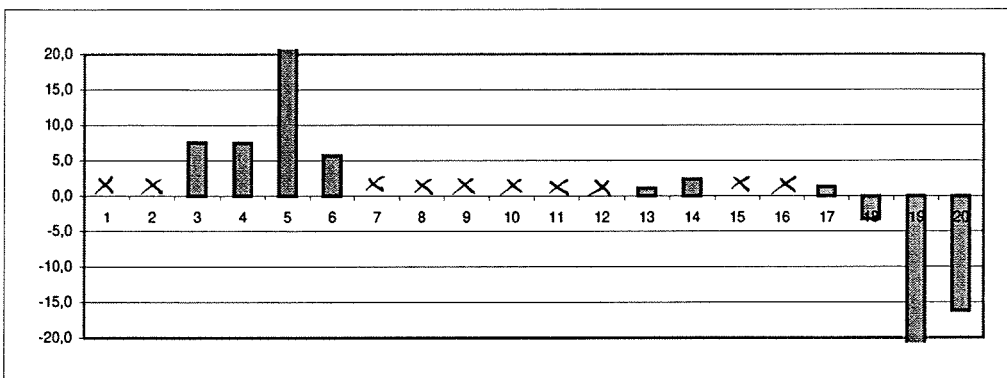
**Aluminium, % relative deviation. Laboratory 5**



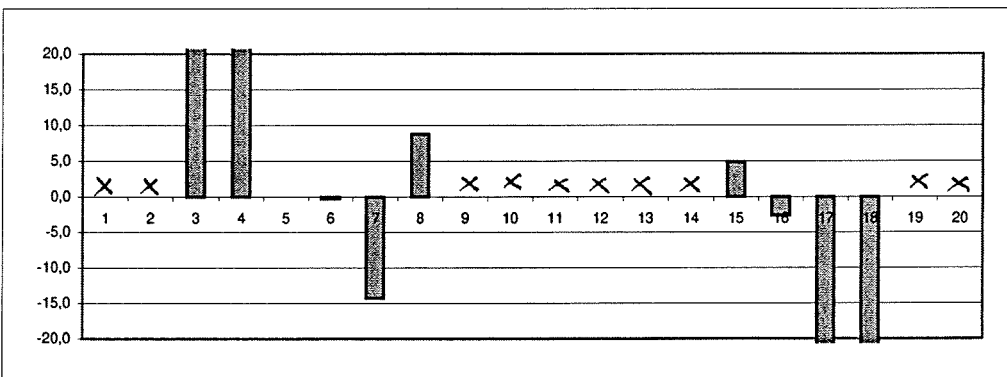
**Aluminium, % relative deviation. Laboratory 6**



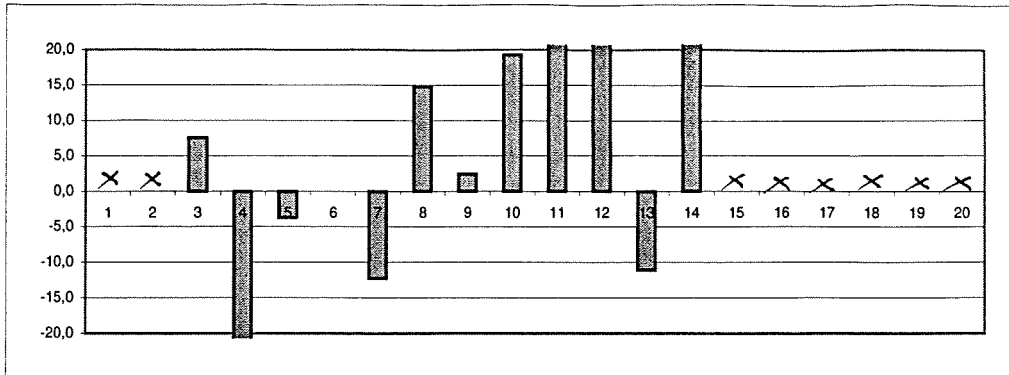
**Aluminium, % relative deviation. Laboratory 7**



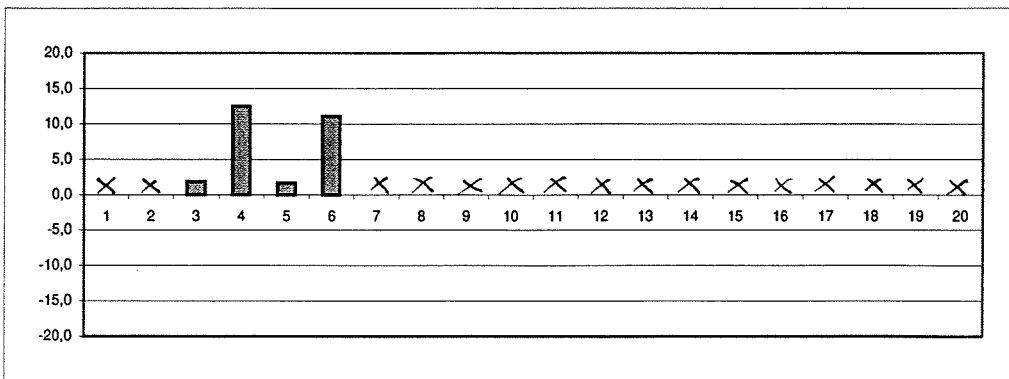
**Aluminium, % relative deviation. Laboratory 8**



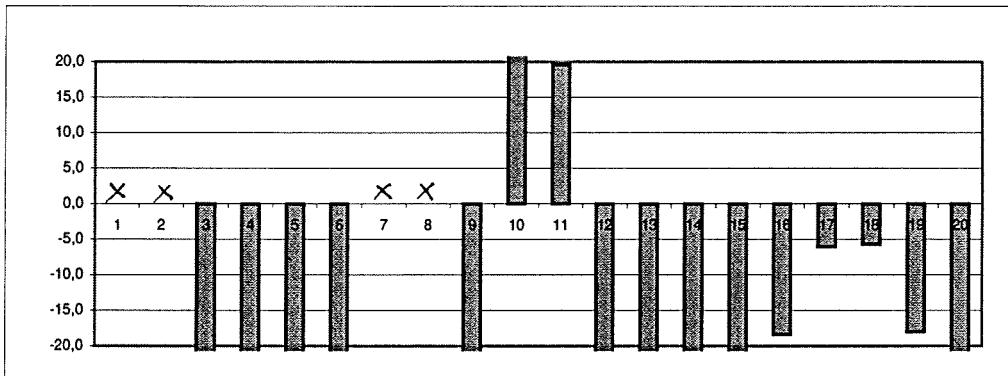
**Aluminium, % relative deviation. Laboratory 9**



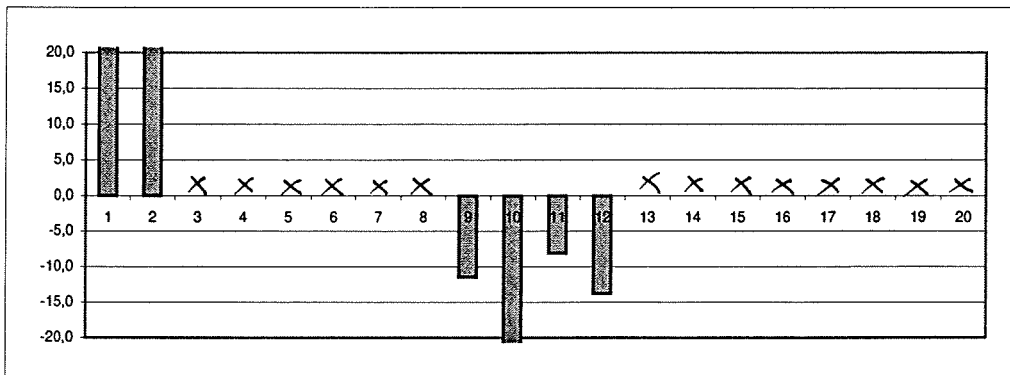
**Aluminium, % relative deviation. Laboratory 10**



**Aluminium, % relative deviation. Laboratory 11**

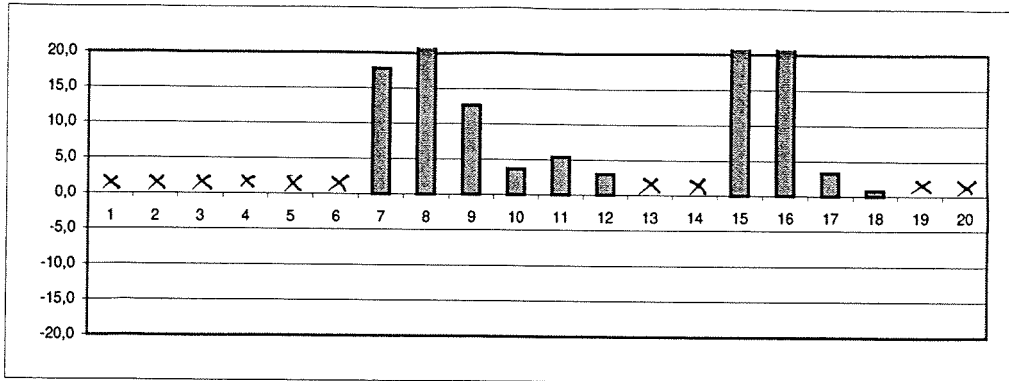


**Aluminium, % relative deviation. Laboratory 13**

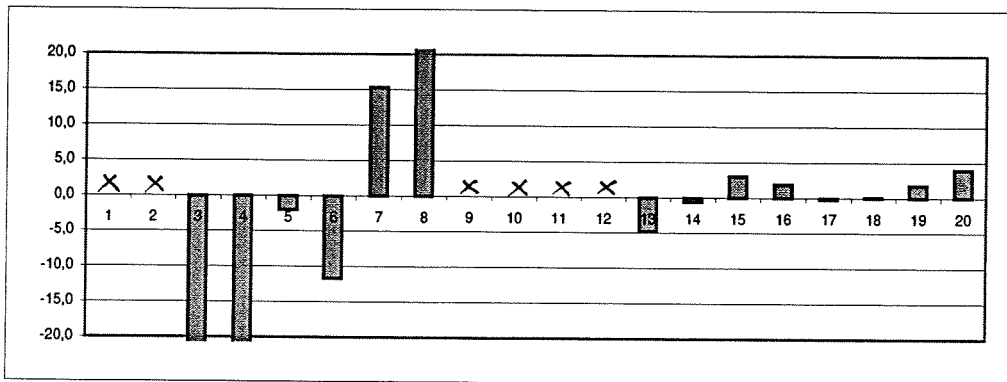




**Aluminium, % relative deviation. Laboratory 14**



**Aluminium, % relative deviation. Laboratory 15**



**Aluminium, % relative deviation. Laboratory 16**

