Determination of metals by atomic absorption spectrometry

Ruggedness test

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Acknowledgdement

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1. INTRODUCTION

The present report covers the activity for Horizontal-Inorg, work package 6, Ruggedness test for a horizontal European standard for determination of trace metals in sewage sludge and comparable matrices.

The ruggedness test is performed for the standard identified during the desk study carried out during Phase I of the present programme (1).

2. MATERIALS

As the determination procedure is strictly given, the possible sensitivity to changes in procedure is closely connected to the variations in the concentrations of other elements and compounds in the digested solutions. The digestion procedure is given elsewhere (2), and the matrix of the solutions are defined by these procedures, dominated by the acid used for the digestion. The acid from the digestion is the dominating part of the matrix, and will be approximately constant for all samples. The varying components in the matrix will be the contributions from the sample itself, this being other metals or anions from the digested sample.

Therefore a series of samples have been prepared with an acid concentration corresponding to the digestion solutions, based on either nitric acid or aqua regia after dilution of the digested sample, as described in the digestion document (2). The different cations to be tested was added as a solution of the nitrate or the chloride salt of the metal to be tested. The anions were taken from a solution of a stoichiometric sodium salt containing the actual anion.

3. DESIGN OF EVALUATION TEST

A working solution containing all the metals to be tested was prepared from 1000 mg/l of commercial stock solutions. The amount of stock solutions added was dependent on the final concentration in the working solution:

Trace metal	Amount of stock solution added, ml	Concentration in working solution, mg/l
Cd	0,2	0,4
Ag	0,5	1,0
Cr, Cu	1,0	2,0
Co. Ni, Pb, V	2,5	5,0

A series of test solutions were prepared in 100 ml volumetric flasks, by adding 1 ml of the working solution to the flasks, the concentration of the trace metal after dilution to the mark will be as given in the second row in Table 1 and 2. The concentration of acid was 25 ml nitric acid in 100 ml, or 7 ml nitric acid and 21 ml hydrochloric acid in 100 ml, respectively, corresponding to the nitric acid and the aqua regia digestion solutions. The ion to be tested for interference was added from a stock solution before diluting to the mark. For a final concentration of 1000 mg/l in the test solution, a volume of 50 ml was taken from a stock solution with concentration 2000 mg/l before dilution to the mark. For final concentrations of 100 mg/l and 10 mg/l, respectively, 5 ml and 0,5 ml of the 2000 mg/l stock solution was added to the 100 ml volumetric flask. The concentration of trace elements and the possible interfering compounds added to the test solutions prepared for testing are given in table 1 and 2 together with the results, for the nitric acid and aqua regia solutions, respectively.

As the digestion acids are the source of the anions nitrate, or a mixture of chloride and nitrate, these ions will be present in approximately constant concentrations in all the samples, and the test with these ions will only include minor variations in their concentrations. The anions to be tested are chloride, bromide, and phosphate. In addition the possible interference from the metals calcium, aluminium, iron, manganese, nickel and cobalt also was tested.

4. RESULTS AND DATA ANALYSIS FOR THE TEST

Table 1. The solutions tested and the measured results for metals in nitric acid solutions.

Metal analysed		**Ag**	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**V**
Concentration µg/l		10	4	50	20	20	50	50	50
Acceptance limits µg/l		9-11	3,6-4,4	45-55	18-22	18-22	45-55	45-55	45-55
Ion added, mg/l	mg/l								
Chloride	10 000	32,4	3,1	40,5	30,4	20,8	20,6	30,0	84,5
	1 000	19,4	3,9	46,3	19,0	18,6	40,6	41,9	57,5
	100	11,0	4,1	50,2	20,8	19,9	49,5	49,9	50,3
Bromide	1 000	7,7	3,5	50,1	19,6	18,4	56,9	42,7	80,5
	100	8,1	3,5	49,5	19,0	18,5	53,3	47,8	50,0
	10	8,9	3,9	49,9	19,7	20,2	60,6	50,6	52,2
Phosphate-P	1 000	15,8	3,4	47,1	22,2	18,0	60,2	33,1	312
	100	10,1	3,7	49,2	19,0	19,9	57,8	44,3	87,0
	10	10,9	3,9	51,0	19,3	20,5	60,7	50,2	60,5
Calcium	1 000	13,3	3,9	49,5	26,2	18,3	53,9	47,8	105
	100	12,0	3,9	51,1	22,3	21,3	50,4	48,7	69,0
	10	10,5	4,1	50,3	21,2	20,1	54,4	49,9	55,0
Aluminium	1 000	25,9	3,8	45,3	81,4	27,8	34,6	33,4	156
	100	21,4	3,8	50,7	23,9	21,3	43,2	52,0	93,5
	10	11,0	4,0	50,1	21,9	20,4	49,2	50,4	52,4
Iron	1 000	7,4	3,6	40,9	226	14,2	30,3	47,7	127
	100	9,0	3,9	53,3	43,1	20,2	32,3	47,3	68,5
	10	10,7	4,2	49,9	25,4	19,9	40,4	49,5	54,0
Manganese	1 000	5,3	4,0	48,8	25,3	19,2	34,8	45,5	117
	100	8,2	3,9	49,8	19,0	19,8	34,4	47,7	65,0
	10	9,5	4,1	49,9	21,4	20,2	54,3	49,8	54,2
Nickel	1 000	10,1	4,1	57,7	23,9	19,4	-	42,2	83,0
	100	10,7	3,9	51,6	20,3	19,1	-	48,0	61,1
	10	9,7	4,0	50,0	22,0	19,8	-	50,5	51,9
Cobalt	1 000	6,1	4,0	-	28,9	21,1	419	45,9	77,2
	100	10,0	3,9	-	21,0	19,1	196	47,5	64,8
	10	10,3	3,9	-	19,7	20,7	89,1	49,9	50,6

Table 2. The solutions tested and the measured results for metals in aqua regia solutions.

Metal analysed		**Ag**	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**V**
Concentration µg/l		10	4	50	20	20	50	50	50
Acceptance limits µg/l		9-11	3,6-4,4	45-55	18-22	18-22	45-55	45-55	45-55
Ion added, mg/l	mg/l								
Chloride	10 000	85,0	1,1	45,0	28,4	18,6	20,6	38,4	248
	1 000	18,3	4,0	52,5	19,5	18,7	40,6	43,8	81,4
	100	14,0	4,0	50,9	18,5	19,9	49,5	48,7	54,4
Bromide	1 000	20,3	3,8	65,1	20,9	19,6	56,9	45,6	66,2
	100	17,9	4,0	54,1	19,7	20,0	53,3	49,3	53,0
	10	14,8	4,0	50,4	18,8	22,3	60,6	49,9	51,0
Phosphate-P	1 000	22,5	3,9	47,2	22,7	17,3	60,2	36,8	176
	100	20,7	3,9	51,3	20,8	20,8	54,8	47,1	63,6
	10	17,2	4,0	52,0	19,5	20,4	50,7	50,1	52,1
Calcium	1 000	12,5	3,9	58,7	24,1	18,1	53,9	46,1	105
	100	16,8	4,0	53,4	20,4	22,4	52,4	49,3	69,4
	10	16,4	3,9	52,4	19,4	21,0	50,4	49,9	59,3
Aluminium	1 000	21,9	3,8	34,2	56,7	15,5	34,6	33,4	502
	100	16,9	3,7	48,0	23,2	22,3	43,2	54,1	93,5
	10	13,9	3,9	50,7	20,4	21,2	49,2	48,4	62,4
Iron	1 000	5,4	3,7	44,1	100	22,9	30,3	46,5	88,3
	100	9,2	3,8	52,7	29,9	21,0	32,3	49,4	61,0
	10	11,2	3,9	45,4	20,3	18,9	40,4	48,4	52,8
Manganese	1 000	6,3	2,7	41,3	24,6	12,0	34,8	42,8	103
	100	10,1	3,9	47,7	17,7	19,7	44,4	49,6	64,6
	10	10,2	4,1	51,3	17,9	21,0	52,3	49,9	55,4
Nickel	1 000	21,7	4,0	33,1	26,5	12,5	-	54,6	202
	100	10,0	3,9	54,7	20,2	18,4	-	50,1	61,6
	10	9,6	4,0	48,9	17,7	18,9	-	49,6	54,6
Cobalt	1 000	11,9	3,2	-	27,9	12,9	419	308	221
	100	9,9	3,8	-	19,8	18,4	196	49,1	64,3
	10	10,4	3,9	-	17,5	20,2	89,1	50,1	55,0

As the digestion procedures are given, either using nitric acid or using aqua regia, the possible content of volatile organic compounds that might have some absorbance in the UV region are removed, and will not cause any problems in the determination step for these metals.

In this study we have defined systematic deviations up to ± 10 % as acceptable, which means that the results for the metals in the test should be within the concentration range given in the third row of the tables 1 and 2.

Cadmium is relatively unaffected by interfering ions in this test. An exception seems to be bromide which reduced the signal in the nitric acid solutions when present in concentrations higher than about 10 mg/l. This should normally not be any big problem as bromide is not expected to be present in higher concentrations in digested solutions of sludges and wastes.

Copper and lead are relatively little influenced by interferences from other ions in these solutions, as a concentration in the range 100 to 1000 mg/l normally is no problem. It seems that there are some effects at lower concentrations in aqua regia solutions than in nitric acid for copper. Normally only high concentrations of other ions may interfere. The same situation we also observe for cobalt.

Nickel is affected more or less by most of the ions tested, the situation being a little more problematic in nitric acid solutions than in aqua regia. The effect is especially pronounced for aluminium, iron, manganese and cobalt. A similar pattern is observed for chromium too, however, the interferences are affecting the absorbance signal at somewhat higher concentrations of the interfering component than for nickel.

Silver and vanadium are effected by many anions and cations being present in concentrations between 10 and 100 mg/l. It is well known that nitric acid reduces the silver signal, however, this should not be any problem here, as the nitric acid concentration is approximately constant in the digested solutions, both in nitric acid digests and in aqua regia digests. For the determination of silver it seems less suitable to use aqua regia digests than nitric acid digests.

In cases where there are interference problems, one way to reduce them is to dilute the sample, provided that the element to be determined is present in sufficiently high concentration. In other cases there may be necessary to apply the technique with standard addition to the digested samples, to reduce the effect of chemical interferences.

5. CONCLUSION

Table 3. Maximum concentrations (in mg/l) of elements which do not interfere in the determination of trace metals in nitric acid solutions.

Metal analysed	**Ag**	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**V**
Concentration µg/l	10	4	50	20	20	50	50	50
Acceptance limits µg/l	9-11	3,6-4,4	45-55	18-22	18-22	45-55	45-55	45-55
Chloride	100	1000	1000	1000	10000	100	100	100
Bromide	10	10	1000	1000	1000	< 10	100	100
Phosphate	100	100	1000	1000	1000	< 10	100	< 10
Calcium	10	1000	1000	100	1000	100	1000	10
Aluminium	10	1000	1000	10	100	10	100	10
Iron	100	1000	100	< 10	100	< 10	1000	10
Manganese	10	1000	1000	100	1000	10	1000	10
Nickel	1000	1000	100	100	1000	-	100	10
Cobalt	100	1000	-	100	1000	< 10	1000	10

Table 4. Maximum concentrations (in mg/l) of elements which do not interfere in the determination of trace metals in aqua regia solutions.

Metal analysed	**Ag**	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**V**
Concentration µg/l	10	4	50	20	20	50	50	50
Acceptance limits µg/l	9-11	3,6-4,4	45-55	18-22	18-22	45-55	45-55	45-55
Chloride	< 100	1000	10000	1000	10000	100	100	100
Bromide	< 10	1000	100	1000	1000	100	1000	100
Phosphate	< 10	1000	1000	1000	100	100	100	10
Calcium	< 10	1000	100	100	1000	1000	1000	< 10
Aluminium	< 10	1000	100	10	100	100	100	< 10
Iron	10	1000	100	10	100	< 10	1000	10
Manganese	100	100	100	10	100	10	100	10
Nickel	100	1000	100	100	100	-	1000	10
Cobalt	100	100	-	100	100	< 10	100	10

In the tables 3 and 4 are given the maximum concentrations of anions and cations which do not lead to greater systematical deviations than about ± 10 %. Depending on the equipment used, and the adjustment of the method used for the determination, there may be observed minor differences from the information given in this table. There are rather small differences between the interference effects observed in nitric acid and aqua regia solutions for the determination of the trace metals in digested solutions.

6. REFERENCES

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