

## Determination of mercury

### Ruggedness test

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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 mercury 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

Mercury has a unique property – it is the only metal exhibiting a considerable vapour pressure at room temperature, the vapour being stable and monoatomic – and it does not react readily with atmospheric oxygen. Hence, mercury produced in elemental form by reduction of its compounds can be entrained in a stream of inert gas, or even air, and measured by the atomic absorption of the cold vapour without the need of either flame or flameless atomizers, or measured by atomic fluorescence.

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 series of solutions were prepared in 100 ml volumetric flasks, 200 µl of a working solution containing 100 µg/l mercury was added to give 0,2 µg/l of mercury in the final solutions. 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. The solutions prepared and tested is 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 therefore fluoride, bromide, iodide, phosphate, and sulfate. In addition the possible interference from the metals arsenic, bismuth, antimony, selenium, silver, aluminium, iron, manganese, copper and zinc also was tested.

#### 4. RESULTS AND DATA ANALYSIS FOR THE TEST

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

Ion	mg/l added	µg/l Hg
Fluoride	100	0,370
	20	0,269
	5	0,250
	1	0,211
	0,1	0,205
Bromide	1000	0,131
	100	0,204
Iodide	0,5	0,250
	0,2	0,230
	0,1	0,216
Sulfate	1000	0,200
	100	0,201
Phosphate	1000	0,207
	100	0,204
Arsenic	100	0,210
	10	0,202
	2	0,206
Bismuth	100	0,214
	10	0,199
	2	0,206
Antimony	100	0,236
	10	0,210
	2	0,208
Selenium	100	0,132
	10	0,191
	2	0,199
Silver	5	0,180
	1	0,194
	0,5	0,200
Aluminium	1000	0,197
	100	0,205
Iron	1000	0,272
	200	0,222
	100	0,200
Manganese	1000	0,196
	10	0,204
Copper	1000	0,189
	100	0,199
Zinc	1000	0,197
	100	0,199



As the digestion procedure is 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 mercury.

Systematic deviations up to  $\pm 5\%$  has been defined as acceptable here, which means that the mercury results in the test should be within the concentration range 0,19 – 0,21 mg/l to be recorded as acceptable. However, in practical life wider limits are very often used.

Even low concentrations of fluoride interfere on the mercury determination, and introduces a strongly positive deviation in the mercury results. At a concentration of 0,1 mg/l the deviation is acceptable. A positive interference is also affected by iodide at very low concentrations, and at a concentration of 0,1 mg/l the deviation is + 8 %. Bromide show a negative deviation at very high concentrations, however, at 100 mg/l the effect is eliminated.

Arsenic at concentrations about 100 mg/l are leading to deviations within acceptable limits, while bismuth and antimony are leading to positive interferences at this concentration level. Selenium leads to strongly negative interferences at a concentration of 100 mg/l, but is acceptable at 10 mg/l.

Some heavy metals lead to systematic interferences, however, this is only in very high concentrations. Thus the positive deviation caused by iron disappears at a concentration of 100 mg/l. An exception is silver, which is leading to negative deviations even at rather low concentrations, at 1 mg/l the effect is reduced to an acceptable level. Most metals up to 100 mg/l do not interfere.

The interferences which occur due to the presence of other elements in the matrix are dependent on the choice of reducing agent. Fewer interferences from heavy metals arise if tin(II) chloride is used rather than sodium tetrahydroborate.

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

Ion	mg/l added	µg/l Hg
Fluoride	10	0,225
	1	0,212
	0,1	0,202
Bromide	1000	0,182
	100	0,190
Iodide	1	0,290
	0,1	0,199
Sulfate	1000	0,212
Phosphate	1000	0,212
Arsenic	10	0,220
	2	0,200
Bismuth	100	0,215
	10	0,208
	1	0,206
Antimony	100	0,226
	10	0,210
	1	0,208
Selenium	100	0,130
	10	0,188
	1	0,196
Silver	5	0,188
	1	0,206
Aluminium	1000	0,196
Iron	1000	0,202
	200	0,199
Manganese	1000	0,198
	10	0,206
Copper	1000	0,197
Zinc	1000	0,199

As for nitric acid digests fluoride interfere even in rather low concentrations, producing a positive deviation in the observed signal. At about 1 mg/l the deviation is within the acceptable limit. Iodide leads to deviating results at even lower concentrations, at 0,1 mg/l the deviation is within the acceptance limit. Bromide in very high concentrations leads to systematically too low results.

Arsenic, bismuth and antimony lead to systematically too high results if present in high concentrations, acceptable results are obtained at concentrations of 10 mg/l or lower. High concentration of selenium leads to systematically low results.

Very few heavy metals lead to systematic interferences, most metals up to 100 mg/l do not interfere. An exception is silver, which is leading to negative deviations even at rather low concentrations, at 1 mg/l the effect is reduced to an acceptable level.

## 5. CONCLUSION

Table 3. Maximum concentrations (in mg/l) of elements which do not interfere in the determination of mercury in nitric acid and aqua regia solutions.

Element	Nitric acid	Aqua regia
Fluoride	1	1
Bromide	100	100
Iodide	0,1	0,1
Sulphate	1000	1000
Phosphate	1000	1000
Arsenic	100	10
Bismuth	100	10
Antimony	10	10
Selenium	10	10
Silver	1	1
Aluminium	1000	1000
Iron	100	1000
Manganese	1000	1000
Copper	1000	1000
Zinc	1000	1000

In table 3 is given the maximum concentrations of elements which do not lead to greater systematical deviations than about  $\pm 5\%$ . Depending on the equipment used there may be observed minor differences from the information given in this table. For this test it was used stannium chloride as reduction agent, sodium tetrahydroborate may lead to somewhat different deviations for some elements.

There are very small differences between the interference effects observed in nitric acid and aqua regia solutions for the determination of mercury in digested solutions.

## 6. REFERENCES

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