RESOLUTION OIV/OENO 344/2010

MULTIELEMENTAL ANALYSIS USING ICP-MS

THE GENERAL ASSEMBLY,

IN VIEW OF Article 2, paragraph 2 of the Agreement of 3 April 2001, Establishing the International Organisation of Vine and Wine;

FURTHER to the proposal of the sub-commission “Methods of Analysis”;

DECIDES to add the following type II method to Appendix A of the “International Compendium of Methods of Analysis”:

Title	Type of method
Multielemental Analysis using ICP-MS	II

1. SCOPE OF APPLICATION

This method can be applied to the analysis of the elements present in wines within the range indicated and featured in the following list:

- Aluminium between 0.25 and 5.0 mg/l
- Boron between 10 and 40 mg/l
- Bromine between 0.20 and 2.5 mg/l
- Cadmium between 0.001 and 0.040 mg/l
- Cobalt between 0.002 and 0.050 mg/l
- Copper between 0.10 and 2.0 mg/l
- Strontium between 0.30 and 1.0 mg/l
- Iron between 0.80 and 5.0 mg/l
- Lithium between 0.010 and 0.050 mg/l
- Magnesium between 50 and 300 mg/l
- Manganese between 0.50 and 1.5 mg/l

Certified in conformity Tbilisi, 25th June 2010
The Director General of the OIV
Secretary of the General Assembly
Frederico CASTELLUCCI

- Nickel between 0.010 and 0.20 mg/l
- Lead between 0.010 and 0.20 mg/l
- Rubidium between 0.50 and 1.2 mg/l
- Sodium between 5 and 30 mg/l
- Vanadium between 0.003 and 0.20 mg/l
- Zinc between 0.30 and 1.0 mg/l

This technique can also be used to analyze other elements.

The sample sometimes requires mineralization. This is the case, for example, of wines with more than 100 g/L of sugar where it can be necessary to realise mineralization of the sample before. In this case, it is recommended to perform a digestion with nitric acid in a microwave.

The technique can also be applied to musts, after mineralization.

2. BASIS

Multielemental quantitative determination using Inductively Coupled Plasma Mass Spectometry or ICP-MS.

Injection and nebulization of the sample in high-frequency plasma. The plasma causes the desolvation, atomization and ionization of the elements in the sample. The ions are extracted using a vacuum system fitted with ionic lenses. The ions are separated according to the mass-to-charge ratio in a mass spectrometer, for example, a quadrupole. Detection and quantification of ions using an electron multiplier system.

3. REAGENTS AND SOLUTIONS

3.1. Ultrapure, demineralized water with resistivity (□ 18 MΩ), in accordance with
ISO 3696.

3.2. Certified solution(s) (for example, 100 mg/l) containing the metals to be analyzed. Multielemental or monoelemental solutions can be used.

3.3. Indium and/or rhodium solution as an internal standard (normally 1 g/l).

3.4. Nitric acid ≥ 60 % (metal impurities □ 0.1 µg/l).

3.5. Argon, minimum purity of 99.999%.

3.6. Nitrogen (maximum impurity content: $H_2O \leq$ 3 mg/l, $O_2 \leq$ 2 mg/l and

$C_nH_m \leq 0.5$ mg/l).

Solution concentration and internal standards are given by way of reference.

Preparation of standard solutions:

Acid concentration in the standards and in the final dilution of the wine samples must be the same and must not exceed 5%. The following is an example.

3.7. Stock solution (5mg/l).

Place 0.5ml of solution (3.2) in a 10 ml (4.5) tube and add 0.1 ml of nitric acid (3.4). Level off to 10 ml with demineralized water (3.1) and homogenize.

Shelf life: 1 month.

3.8. Internal standard solution (1 mg/l).

Using micropipettes (4.4), place 50 µl of indium or rhodium solution (3.3) and 0.5 ml of nitric acid (3.4) in a 50 ml tube (4.6). Level off to 50 ml with demineralized water (3.1) and homogenize.

Shelf life: 1 month.

3.9. Standard solutions of the calibration curve.

Adapt the range of the series of standards according to the dilution on the sample or the equipment used.

Use 1000 µl and 100 µl pipettes (4.4).

Shelf life of standard solutions: 1 day

These standard solutions can also be prepared gravimetrically.

Add internal standard in the same concentration as for the samples.

3.10. Internal control wine of known concentrations (MRC, MRE, MRI, etc.).

4. MATERIAL AND EQUIPMENT

4.1. Inductively coupled mass spectrometer with/without collision/reaction cell.

4.2. Computer with data processing software and printer.

4.3. Autosampler (optional).

4.4. 1000 µl and 100 µl micropipettes.

4.5. 10 ml plastic, graduated test tubes with bung or glass volumetric flasks.

4.6. 50 ml plastic, graduated test tubes with bung or glass volumetric flasks.

All volumetric material (micropipettes and test tubes) must be duly calibrated.

Note: material that will come into contact with the sample, such as, for example, tubes and tips, must remain for at least 24 hours in a nitric acid solution (3.4) at a concentration of 10% and must subsequently be rinsed several times in water (3.1).

5. SAMPLE PREPARATION

Samples of sparkling wine must be degasified. This can be done through nitrogen bubbling (3.6) for 10 minutes or by using an ultrasound bath.

Remove the bung carefully to ensure that the wine is not contaminated. Wash the bottle neck in an acid solution (2%HNO_3). Wine samples are taken directly from the bottle.

Use a micropipette (4.4) to insert 0.5 ml of wine, 0.1 to 0.5 ml of nitric acid (3.4) and 100 µl of internal standard solution (3.8) into a 10 ml tube (3.5).Level off with water (3.1) and homogenize.

For certain elements a higher dilution may be necessary owing to their high natural content in the sample.

Br has high ionization potential and its ionization in plasma may be incomplete because of the presence of high concentrations of other elements in wines with low ionization potential. This may result in the incorrect quantification of Br and therefore a 1/50 dilution is recommended to avoid this effect (in the event of another dilution being used, confirm the results by checking recovery after an addition).

When the standards are prepared gravimetrically, the final dilution of the sample must also be obtained gravimetrically.

6. PROCEDURE

Switch on the device (pump working and plasma on).

Clean the system for 20 minutes using 2% nitric acid (3.4).

Check that the device is functioning correctly.

Analyze a blank and the series of standard solutions in increasing concentrations, then a standard solution (e.g. no. 2 of series 3.9) to check for correct calibration and finally the blank to ensure that there is no memory effect. Read the samples in duplicate. For the internal control, use a wine of known concentrations (3.10) to confirm that the results are coherent.

Element	m/z*
Aluminium	27

Element	m/z*
Boron	11
Bromine	79
Cadmium	114
Cobalt	59
Copper	63
Strontium	88
Iron	56/57
Lithium	7
Magnesium	24
Manganese	55
Nickel	60
Lead	average of 206, 207 and 208
Rubidium	85
Sodium	23
Vanadium	51
Zinc	64

*The above table is given by way of example. Other isotopes may be required, depending on the equipment.

In the event of using equipment with no collision/reaction cell, correction equations may be necessary for some elements.

7. RESULTS

The software can calculate the results directly.

Element concentrations are reported in mg/l to two decimal points.

Obtain, by interpolating in the calibration curve, the concentration of the elements in the diluted samples. Use the following equation to calculate the concentration of the elements in the sample:

$$C = \frac{C_m \times V_t}{V_m}$$

Where:

- C = Concentration of the element in the sample
- C_m= Concentration of the elements in the diluted sample
- V_t= Final volume of the measurement solution, in ml
- V_m= Aliquot volume of wine, in ml.

8. QUALITY CONTROL

Ensure traceability by using certified standards.

In each analytical series, use a CRM (Certified Reference Material) as an internal control of wine or a wine used as reference material from an interlaboratory test campaign.

It is recommended that control graphs be created from the results of the quality control analysis.

Participation in interlaboratory test campaigns.

9. PRECISION

The results of the statistical parameters of the collaborative trial are shown in Appendix A.

9.1. Repeatability (r)

The difference between two independent results, obtained using the same method, in the same sample, in the same laboratory, by the same operator, using the same equipment in a short time interval. r results are given in Tables 1 to 17 of Appendix A

9.2. Reproducibility (R)

The difference between two results, obtained using the same method, in the same sample, in a different laboratory, by a different operator and with different equipment. R results are given in Tables 1 to 17 of the Appendix A.

Table 1 represents the % of the relative standard deviation of Repeatability and Reproducibility (RSDr% et RSDR%) of the method.

(*) C = Concentration

Element	Concentration	RSD_r %	RSD_R %
Aluminium	0,25 – 5,0 mg/l	4	10
Boron	10 - 40 mg/l	3,8	6,3
Bromine	0,20– 1,0 mg/l	4,1	16,3
	≥ 1,0 – 2,5 mg/l	2.1	8,0
Cadmium	0,001 – 0,020 mg/l	0,06 C*+0,18	10
	≥ 0,020 – 0,040 mg/l	1,5	10
Cobalt	0,002 – 0,050 mg/l	3,2	13,2
Copper	0,10 – 0,50 mg/l	3,8	11,4
	≥ 0,50 – 2,0 mg/l	2,0	11,4
Strontium	0,30 – 1,0 mg/l	2,5	7,5

Iron	0,80– 1,0 mg/l	4,2	15,7
	≥ 1,0-5,0 mg/l	4,2	7,8
Lithium	0,010 – 0,050 mg/l	7	12
Magnesium	50 - 300 mg/l	2	6
Manganese	0,50-1,5 mg/l	3	7
Nickel	0,010 – 0,20 mg/l	5	8
Lead	0,010 – 0,050 mg/l	8	7
	≥ 0,050 – 0,20 mg/l	2	7
Rubidium	0,50 – 1,2 mg/l	3	6
Sodium	5 - 10 mg/l	2	10
	≥ 10 - 30 mg/l	0,3 C*-2,5	10
Vanadium	0,003 – 0,010 mg/l	8	10
	≥ 0,010 – 0,20 mg/l	3	10
Zinc	0,30 – 1,0 mg/l	5	12

Table 1: relative standard deviation of Repeatability and Reproducibility

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APPENDIX A

RESULTS OF THE COLLABORATIVE TRIALS

The method has been checked with two collaborative trials, by evaluating precision in accordance with ISO 5725.The trueness of the method has been obtained through recovery studies.

1st Collaborative Trial

8 samples (A, B, C, D, E, F, MH1 and MH2) were used from the following origins:

- Three samples of red wine, with and without addition.
- Three samples of white wine, with and without addition.
- Two samples of synthetic hydroalcoholic mixture, prepared with ethanol and water.

Hydroalcoholic sample MH1 presented problems of instability during the trial and the results have not been taken into account.

	MH2	A	B	C	D	E	F
Metal (mg/l)	Hydroalcoholic mixture	RW2	RW3	WW2	WW3	Natural red wine	Natural white wine
Aluminium	5	0.5	2	2	1	No addition	No addition
Cadmium	0.001	0.005	0.02	0.05	0.01	No addition	No addition
Strontium	0.300	No addition	No addition	No addition	No addition	No addition	No addition
Lithium	0.020	0.01	0.02	0.04	0.01	No addition	No addition
Magnesium	50	100	200	50	25	No addition	No addition
Manganese	0.500	0.5	1	1	0.5	No addition	No addition
Nickel	0.070	0.025	0.2	0.1	0.1	No addition	No addition
Lead	0.010	0.05	0.1	0.15	0.05	No addition	No addition
Rubidium	1.0	No addition	No addition	No addition	No addition	No addition	No addition
Sodium	20	10	10	20	5	No addition	No addition
Vanadium	0.010	0.05	0.2	0.1	0.1	No addition	No addition
Zinc	0.500	0.1	1	0.5	0.5	No addition	No addition

2nd Collaborative Trial

Sixteen samples (A, B, C, D, E, F, G, H, I, J, K, L, M, N, O, P) from the following origins were used:

- Four samples of red wine, with and without addition.
- Four samples of Port wine, with and without addition.
- Six samples of white wine, with and without addition.
- Two samples of champagne.

Amounts added to the samples

Samples	Code	Addition	B	Co	Cu	Fe
			mg/l	µg/l	mg/l	Mg/l
White wine	F-N	No addition	0.0	0.0	0.0	0.0
	C-I	Addition 1	5.0	5.0	5.0	1.0
	A-O	Addition 2	10.0	10.0	1.0	2.0
Liqueur wine	B-K	No addition	0.0	0.0	0.0	0.0
	E-L	Addition 3	15.0	20.0	1.5	3.0
Red wine	D-M	No addition	0.0	0.0	0.0	0.0
	H-J	Addition 4	20.0	50.0	2.0	5.0
Sparkling wine	G-P	No addition	0.0	0.0	0.0	0.0

PRECISION PARAMETERS (Tables 1 to 17):

The values of Horratr and HorratR have been obtained by using the Horwitz equation taking into account Thompson’s modification for the concentration below 120 µg/L.

Table 1: Aluminium (mg/l)

SAMPLE:	LAB. No.	Accepted	Vréf	Sr	r	RSD$_r$(%)	Horwitz RSD$_r$ (%)	Horrat$_r$	SR	R	RSD$_R$ (%)	Horwitz$_R$ RSD$_R$ (%)	Horrat$_R$
A	11	10	0,68	0,020	0,06	2,9	11	0,26	0,077	0,22	11	17	0,66
B	11	9	2,1	0,043	0,12	2,0	9,4	0,22	0,21	0,61	10	14	0,71
C	11	9	2,1	0,032	0,09	1,5	9,5	0,16	0,21	0,59	10	14	0,69
D	11	10	1,2	0,041	0,12	3,4	10	0,34	0,10	0,29	8,3	16	0,56
E	11	10	0,34	0,014	0,04	4,1	12	0,34	0,029	0,08	8,5	19	0,46
F	11	10	0,27	0,006	0,02	2,2	13	0,17	0,028	0,08	10	20	0,52
MH2	11	8	5,2	0,26	0,73	5,0	8,2	0,60	0,56	1,6	11	13	0,86

Table 2: Boron (mg/l)

SAMPLE:	LAB. No.	Accepted	Vréf	Sr	r	RSD$_r$(%)	Horwitz RSD$_r$ (%)	Horrat$_r$	SR	R	RSD$_R$ (%)	Horwitz$_R$ RSD$_R$ (%)	Horrat$_R$
A-O	8	6	18	0,77	2,2	4,3	6,8	0,62	0,94	2,69	5,2	10	0,50
B-K	8	4	4,5	0,27	0,76	6,0	8,4	0,72	0,40	1,14	8,9	13	0,70
C-I	8	4	13	0,31	0,89	2,4	7,2	0,33	0,33	0,94	2,5	11	0,24
D-M	8	7	11	0,26	0,74	2,4	7.4	0,31	1,1	3,11	10	11	0,90
E-L	8	5	21	0,47	1,3	2,2	6.7	0,33	0,85	2,43	4,0	10	0,40
F-N	8	5	8,3	0,43	1,2	5,2	7.7	0,68	0,47	1,34	5,7	12	0,48
G-P	7	4	3,1	0,094	0,27	3,0	8.9	0,34	0,18	0,51	5,8	14	0,43
H-J	8	5	31	1,0	3,0	3,2	6.3	0,54	1,6	4,43	5,2	9,6	0,52

Table 3: Bromine (mg/l

SAMPLE:	LAB. No.	Accepted	Vref	Sr	r	RSD$_r$(%)	Horwitz RSD$_r$ (%)	Horrat$_r$	SR	R	RSD$_R$ (%)	Horwitz$_R$ RSD$_R$ (%)	Horrat$_R$
A-O	6	2	1,21	0,028	0,08	2,3	10,3	0,22	0,041	0,12	3,4	15,6	0,22

B-K	5	2	0,19	0,006	0,02	2,9	13,6	0,21	0,0043	0,012	2,3	20,5	0,11
C-I	6	3	0,81	0,017	0,05	2,1	10,9	0,19	0,062	0,18	7,7	16,5	0,47
D-M	6	4	0,38	0,017	0,05	4,5	12,2	0,37	0,066	0,19	17,4	18,5	0,94
E-L	6	3	1,72	0,030	0,09	1,7	9,7	0,17	0,22	0,62	12,8	14,8	0,86
F-N	6	3	0,22	0,014	0,04	6,4	13,3	0,48	0,046	0,13	20,9	20,1	1
H-J	6	2	2,30	0,061	0,17	2.7	9,3	0,28	0,092	0,26	4	14.1	0.28

Table 4: Cadmium (µg/l)

SAMPLE:	LAB. No.	Accepted	Vréf	Sr	r	RSD $_r$ (%)	Horwitz RSD$_r$ (%)	Horrat$_r$	SR	R	RSD$_R$ (%)	Horwitz$_R$ RSD$_R$ (%)	Horrat$_R$
A	12	11	6	0,2	0,6	3,3	15	0,22	1	3	17	22	0,77
B	12	11	16	0,4	1	2,5	15	0,17	2	6	13	22	0,59
C	12	9	40	0,4	1	1,0	15	0,07	3	8	7,5	22	0,34
D	12	10	10	0,3	0,8	3,0	15	0,20	0,9	3	9,0	22	0,41
E	8	7	0,3	0,20	0,6	67	15	4,47	0,20	0,67	67	22	3,05
F	8	6	0,3	0,04	0,1	13	15	0,87	0,20	0,45	67	22	3,05
MH2	9	5	0,9	0,08	0,2	8,9	15	0,59	0,10	0,29	11	22	0,50

Table 5: Cobalt (µg/l)

SAMPLE:	LAB. No.	Accepted	Vréf	Sr	r	RSD $_r$ (%)	Horwitz RSD$_r$ (%)	Horrat$_r$	SR	R	RSD$_R$ (%)	Horwitz$_R$ RSD$_R$ (%)	Horrat$_R$
A-O	10	6	22	0,5	1	2,3	15	0,15	2	6	9,1	22	0,41
B-K	10	6	8	0,3	0,9	3,8	15	0,25	1	4	13	22	0,59
C-I	10	8	19	0,4	1	2,1	15	0,14	3	7	16	22	0,73
D-M	10	3	3	0,07	0,2	2,3	15	0,15	0,1	0,3	3,3	22	0,15
E-L	10	8	27	1	3	3,7	15	0,25	3	9	11	22	0,50
F-N	10	7	12	0,5	2	4,2	15	0,28	1	4	8,3	22	0,38
G-P	9	5	2	0,2	0,5	10	15	0,67	0,3	0,8	15	22	0,68
H-J	10	6	49	0,5	1	2,3	15	0,15	6	18	12	22	0,55

Table 6: Copper (mg/l)

SAMPLE:	LAB. No.	Accepted	Vréf	Sr	r	RSD $_r$(%)	Horwitz RSD$_r$ (%)	Horrat$_r$	SR	R	RSD$_R$ (%)	Horwitz$_R$ RSD$_R$ (%)	Horrat$_R$
A-O	10	8	1,1	0,013	0,040	1,2	10	0,12	0,11	0,32	10	16	0,63
B-K	10	8	0,21	0,006	0,020	2,9	13	0,22	0,021	0,060	10	20	0,50
C-I	10	7	0,74	0,009	0,030	1,2	10	0,12	0,046	0,13	6,2	17	0,36
D-M	10	8	0,14	0,007	0,020	5,0	14	0,36	0,015	0,043	11	22	0,50
E-L	10	9	1,7	0,061	0,17	3,6	7,8	0,5	0,16	0,46	9,0	15	0,60
F-N	10	7	0,16	0,006	0,020	3,8	14	0,27	0,029	0,083	18	21	0,86
G-P	9	4	0,042	0,004	0,010	9,5	15	0,63	0,006	0,017	14	22	0,64
H-J	10	7	2,1	0,018	0,050	0,86	9,5	0,09	0,24	0,69	11	14	0,79

Table 7: Strontium (µg/l)

SAMPLE	LAB. N°	Accepted	Vréf	Sr	r	RSD $_r$(%)	Horwitz RSD$_r$ (%)	Horrat$_r$	SR	R	RSD$_R$ (%)	Horwitz$_R$ RSD$_R$ (%)	Horrat$_R$
A	12	11	1091	33	93	3,0	10	0,30	78	222	7,2	16	0,45
B	12	8	1139	66	188	5,8	10	0,58	69	195	6,1	16	0,38
C	12	9	328	6	18	1,8	13	0,14	19	54	5,8	19	0,31
D	12	10	313	7	20	2,2	13	0,17	22	61	7,0	19	0,37
E	12	10	1176	28	80	2,4	10	0,24	86	243	7,3	16	0,46
F	12	10	293	3	9	1,0	13	0,08	22	62	7,5	19	0,39
MH2	12	9	352	7	19	2,0	12	0,17	24	69	6,8	19	0,36

Table 8: Iron (mg/l)

SAMPLE:	LAB. No.	Accepted	Vréf	Sr	r	RSD $_r$(%)	Horwitz RSD$_r$ (%)	Horrat$_r$	SR	R	RSD$_R$ (%)	Horwitz$_R$ RSD$_R$ (%)	Horrat$_R$
A-O	10	6	3,2	0,017	0,05	0,53	8,9	0,06	0,23	0,66	7,2	13	0,55

B-K	10	6	1,5	0,085	0,24	5,7	9,9	0,58	0,11	0,31	7,3	15	0,49
C-I	10	5	2,1	0,036	0,10	1,7	9,4	0,18	0,18	0,51	8,6	14	0,61
D-M	10	5	3,1	0,033	0,094	1,1	8,9	0,12	0,29	0,83	9,4	14	0,67
E-L	10	5	4,3	0,120	0,34	2,8	8,5	0,33	0,29	0,83	6,7	13	0,52
F-N	10	6	1,1	0,051	0,15	4,6	10	0,46	0,16	0,46	15	16	0,94
G-P	9	6	0,83	0,024	0,07	2,9	11	0,26	0,14	0,40	17	16	1,06
H-J	10	7	7,8	0,180	0,52	2,3	7,8	0,29	1,2	3,52	15	12	1,25

Table 9: Lithium (µg/l)

SAMPLE:	LAB. No.	Accepted	Vréf	Sr	r	RSD $_r$(%)	Horwitz RSD$_r$ (%)	Horrat$_r$	SR	R	RSD$_R$ (%)	Horwitz$_R$ RSD$_R$ (%)	Horrat$_R$
A	11	10	34	2	5	5,9	15	0,39	4	11	11	22	0,50
B	11	11	42	3	8	7,1	15	0,47	4	12	10	22	0,45
C	11	11	47	1	4	2,1	15	0,14	5	13	9,8	22	0,45
D	11	11	18	1	4	5,6	15	0,37	2	7	14	22	0,64
E	11	11	25	1	3	4,0	15	0,27	3	9	12	22	0,55
F	11	9	9	0,3	1	3,8	15	0,25	0,6	2	7,2	22	0,33
MH2	11	7	22	1	3	4,6	15	0,31	1	3	5,3	22	0,24

Table 10: Magnesium (mg/l)

SAMPLE:	LAB. No.	Accepted	Vréf	Sr	r	RSD $_r$(%)	Horwitz RSD$_r$ (%)	Horrat$_r$	SR	R	RSD$_R$ (%)	Horwitz$_R$ RSD$_R$ (%)	Horrat$_R$
A	10	7	182	2,9	8,1	1,6	4,3	0,37	9,3	26	5,1	7,3	0,70
B	10	6	280	3,9	11	1,4	4,5	0,31	6,0	17	2,1	6,9	0,30
C	10	7	104	2,4	6,9	2,3	5,3	0,43	6,8	19,25	6,5	8,0	0,81
D	10	6	85	1,4	4,0	1,7	5,4	0,31	2,2	6,1	2,6	8,2	0,32
E	10	7	94	2,2	6,2	2,3	5,3	0,43	5,5	16	5,9	8,1	0,73
F	10	7	65	0,95	2,7	1,5	5,6	0,27	3,8	11	5,9	8,5	0,69
MH2	10	7	51	0,90	2,5	1,8	5,8	0,31	2,4	6,9	4,7	8,9	0,53

Table 11: Manganese (mg/l)

SAMPLE:	LAB. No.	Accepted	Vréf	Sr	r	RSD $_r$(%)	Horwitz RSD$_r$ (%)	Horrat$_r$	SR	R	RSD$_R$ (%)	Horwitz$_R$ RSD$_R$ (%)	Horrat$_R$
A	11	10	1,3	0,014	0,040	1,1	10	0,11	0,13	0,37	10	15	0,67
B	11	9	1,8	0,14	0,40	7,8	9,7	0,80	0,20	0,56	11	15	0,73
C	11	8	1,5	0,028	0,080	1,9	9,9	0,19	0,084	0,24	5,6	15	0,37
D	11	8	1,0	0,035	0,10	3,5	11	0,32	0,049	0,14	4,9	16	0,31
E	11	9	0,84	0,019	0,050	2,3	11	0,21	0,057	0,16	6,8	16	0,43
F	11	9	0,59	0,015	0,040	2,5	11	0,23	0,031	0,090	5,3	17	0,31
MH2	11	8	0,52	0,029	0,080	5,6	12	0,47	0,037	0,10	7,1	18	0,39

Table 12: Nickel (µg/l)

SAMPLE:	LAB. No.	Accepted	Vréf	Sr	r	RSD $_r$(%)	Horwitz RSD$_r$ (%)	Horrat$_r$	SR	R	RSD$_R$ (%)	Horwitz$_R$ RSD$_R$ (%)	Horrat$_R$
A	11	10	40	2	6	5,0	15	0,33	5	13,90	13	22	0,59
B	12	10	194	7	20	3,6	14	0,26	17	48,96	8,8	21	0,42
C	12	8	148	4	10	2,7	14	0,19	5	15,12	3,4	21	0,16
D	12	8	157	4	12	2,6	14	0,19	8	23,10	5,1	21	0,24
E	11	8	15	0,6	2	4,0	15	0,27	1	3,33	6,7	22	0,30
F	12	9	66	1	4	1,5	15	0,10	4	10,58	6,1	22	0,28
MH2	11	7	71	5	14	7,0	15	0,47	4	11,41	5,6	22	0,25

Table 13: Lead (µg/l)

SAMPLE:	LAB. No.	Accepted	Vréf	Sr	r	RSD $_r$(%)	Horwitz RSD$_r$ (%)	Horrat$_r$	SR	R	RSD$_R$ (%)	Horwitz$_R$ RSD$_R$ (%)	Horrat$_R$
A	12	9	59	1	4	1,7	15	0,11	3	9	5,1	22	0,23
B	12	10	109	2	6	1,8	15	0,12	8	23	7,3	22	0,33
C	12	9	136	3	9	2,2	14	0,16	13	37	9,6	22	0,44
D	12	9	119	2	6	1,7	15	0,11	5	13	4,2	22	0,19
E	12	10	13	1	3	7,7	15	0,51	1	4	7,7	22	0,35

F	12	9	92	1	4	1,1	15	0,07	4	11	4,4	22	0,20
MH2	12	10	13	1	3	7,7	15	0,51	1	3	7,7	22	0,35

Table 14: Rubidium (µg/l)

SAMPLE:	LAB. No.	Accepted	Vréf	Sr	r	RSD $_r$(%)	Horwitz RSD$_r$ (%)	Horrat$_r$	SR	R	RSD$_R$ (%)	Horwitz$_R$ RSD$_R$ (%)	Horrat$_R$
A	11	6	717	14	41	2,0	11	0,18	13	36	1,8	17	0,11
B	11	7	799	25	70	3,1	11	0,28	30	86	3,8	17	0,22
C	11	8	677	10	27	1,5	11	0,14	34	96	5,0	17	0,29
D	11	7	612	18	51	2,9	11	0,26	18	50	2,9	17	0,17
E	11	9	741	19	53	2,6	11	0,24	66	187	8,9	17	0,52
F	11	9	617	10	28	1,6	11	0,15	43	123	7,0	17	0,41
MH2	11	7	1128	10	28	0,89	10	0,09	64	181	5,7	16	0,36

Table 15: Sodium (mg/l)

SAMPLE:	LAB. No.	Accepted	Vréf	Sr	r	RSD $_r$(%)	Horwitz RSD$_r$ (%)	Horrat$_r$	SR	R	RSD$_R$ (%)	Horwitz$_R$ RSD$_R$ (%)	Horrat$_R$
A	10	9	19	0,59	1,7	3,1	6,8	0,46	2,2	5,7	12	10	1,20
B	10	9	20	1,3	3,6	6,5	6,7	0,97	2,2	6,3	11	10	1,10
C	10	7	28	0,33	0,93	1,2	6,4	0,19	1,9	5,4	6,8	9,7	0,70
D	10	8	11	0,24	0,68	2,2	7,4	0,30	1,1	3,0	10	11	0,91
E	10	8	9,8	0,19	0,53	1,9	7,5	0,25	0,89	2,5	9,1	11	0,83
F	10	8	6,1	0,093	0,26	1,5	8,1	0,19	0,74	2,1	12	12	1,00
MH2	10	8	24	1,8	5,0	7,5	6,6	1,14	2,6	7,2	11	9,9	1,11

Table 16: Vanadium (µg/l)

SAMPLE:	LAB. No.	Accepted	Vréf	Sr	r	RSD $_r$(%)	Horwitz RSD$_r$ (%)	Horrat$_r$	SR	R	RSD$_R$ (%)	Horwitz$_R$ RSD$_R$ (%)	Horrat$_R$
A	12	11	46	1	3	2,2	15	0,15	5	13	11	22	0,50

B	12	11	167	5	15	3,0	14	0,21	19	54	11	21	0,52
C	12	11	93	3	8	3,2	15	0,21	12	33	13	22	0,59
D	12	9	96	3	8	3,1	15	0,21	8	22	8,3	22	0,38
E	10	7	3	0,2	0,7	6,7	15	0,45	0,3	0,9	10	22	0,45
F	10	8	3	0,2	0,6	6,7	15	0,45	0,2	0,7	6,7	22	0,30
MH2	12	9	11	0,3	1	2,7	15	0,18	0,9	3	8,2	22	0,37

Table 17: Zinc (µg/l)

SAMPLE:	LAB. No.	Accepted	Vréf	Sr	r	RSD $_r$ (%)	Horwitz RSD$_r$ (%)	Horrat$_r$	SR	R	RSD$_R$ (%)	Horwitz$_R$ RSD$_R$ (%)	Horrat$_R$
A	11	8	405	22	61	5,4	12	0,45	45	128	11	18	0,61
B	11	9	1327	49	138	3,7	10	0,37	152	429	11	15	0,73
C	11	9	990	14	41	1,4	11	0,13	86	243	8,7	16	0,54
D	11	9	1002	28	79	2,8	11	0,25	110	310	11	16	0,69
E	11	9	328	13	37	4,0	13	0,31	79	224	24	19	1,26
F	11	9	539	15	42	2,8	12	0,23	61	172	11	18	0,61
MH2	11	8	604	72	204	12	11	1,09	89	251	15	17	0,88