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Primary methods

Determination of the analyte mass concentration

in single element water calibration solutions

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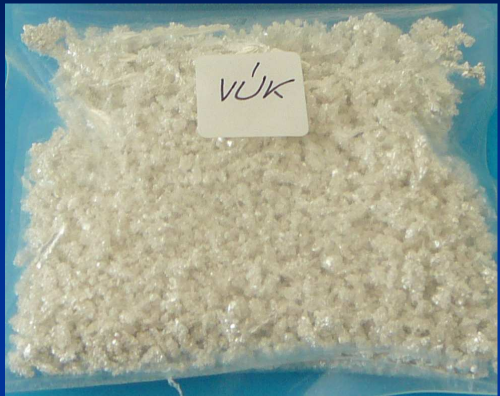
Gravimetric preparation of water calibration solutions and analyte mass concentration determination



$$\gamma(A) \pm U$$

Sodium calibration solution in 2% (v/v) nitric acid (Kragten spreadsheet)

Sodium std. solution in 2% nitric acid	Average sample weight	Volume of the sample analysed (std. solution)	Gravimetric factor	Repeatability of the analysis
	a [g]	**b [ml]**	**c [1]**	**repeatability [1]**
Value	0,30913	10,01	0,3237035	1
Uncertainty	0,00007	0,00087	0,0000068	0,000388
a [g]	0,30920	0,30913	0,30913	0,30913
b [ml]	10,01	10,01087	10,01	10,01
c [1]	0,3237035	0,3237035	0,3237103	0,3237035
repeatability [1]	1	1	1	1,000388
Mass conc. (γ(u)), [mg/l]	9998,8	9995,7	9996,8	10000,4
γ(average) - γ(u), [mg/l]	-2,264	0,869	-0,209	-3,882
(γ(av.) - γ(u))2, [mg/l]2	5,124	0,755	0,044	15,073
Contribution to the total u	24,4%	3,6%	0,2%	71,8%
Σ(γ(av.) - γ(u))2, [mg/l]2	20,99537			**100,00%**
Total uncertainty u, [mg/l]	**4,6**	Average mass concentration	**9996,6**	[mg/l]
Expanded comb. U, [mg/l]	**9,2**	U, k=2	**9,2**	[mg/l]
Repeatability of the method	**0,12%**	Ref. mass conecntration	**10000,0**	[mg/l]
Recovery (rel.)	**99,97%**	U, k=2	**20,0**	[mg/l]
Recovery uncertainty (rel.)	**0,11%**	u	**10,0**	[mg/l]
γ(average) - γ(ref.)	**3,4**	[mg/l]	Metrological compatibility [mg/l]	
u (γ(average) - γ(ref.))	**11,0**	[mg/l]	γ(average) - γ(ref.)	U (γ(average) - γ(ref.))
U (γ(average) - γ(ref.))	**22,0**	[mg/l]	**3,4**	**22,0**

Antimony calibration solution in 1%HF+5%HNO_3 (v/v)

Antimony std. solution in 1% hydrofluoric + 5% nitric acid	Weight of potassium bromate for the volumetric solution	Purity of potassium bromate for the vol. solution preparation	Molar mass of potassium bromate	Volume of potassium bromate volumetric solution	Volume of the sample analysed (antimony std. solution)	Volume of potassium bromate vol. solution during the titration	Molar mass of antimony	Repeatability of the analysis
	a [g]	**P [1]**	**b [g/mol]**	**c [ml]**	**d [ml]**	**e [ml]**	**f [g/mol]**	**repeatability**
Value	1,66992	1	167,0005	1000	99,94	27,41	121,76	1
Uncertainty	0,00007	0,000115	0,000779	0,1915	0,0112	0,0062	0,000577	0,000413
a	1,66999	1,66992	1,66992	1,66992	1,66992	1,66992	1,66992	1,66992
P	1	1,000115	1	1	1	1	1	1
b	167,0005	167,0005	167,001279	167,0005	167,0005	167,0005	167,0005	167,0005
c	1000	1000	1000	1000,1915	1000	1000	1000	1000
d	99,94	99,94	99,94	99,94	99,9512	99,94	99,94	99,94
e	27,41	27,41	27,41	27,41	27,41	27,41245	27,41	27,41
f	121,76	121,76	121,76	121,76	121,76	121,76	121,760577	121,76
repeatability	1	1	1	1	1	1	1	1,000413
Mass conc. (γ(u)), [mg/l]	1001,69	1001,76	1001,64	1001,45	1001,53	1001,87	1001,65	1002,06
γ(average) - γ(u), [mg/l]	-0,042	-0,116	0,005	0,192	0,112	-0,227	-0,005	-0,414
(γ(av.) - γ(u))2, [mg/l]2	0,002	0,013	0,000	0,037	0,013	0,051	0,000	0,171
Contribution to the total u	**0,6%**	**4,7%**	**0,0%**	**12,8%**	**4,4%**	**17,9%**	**0,0%**	**59,7%**
Σ(γ(av.) - γ(u))2, [mg/l]2	0,287							**100,0%**
Total uncertainty u, [mg/l]	**0,54**	Average mass concentration		**1001,6**	[mg/l]			
U (k=2), [mg/l]	**1,07**		U (k=2)	**1,1**	[mg/l]			

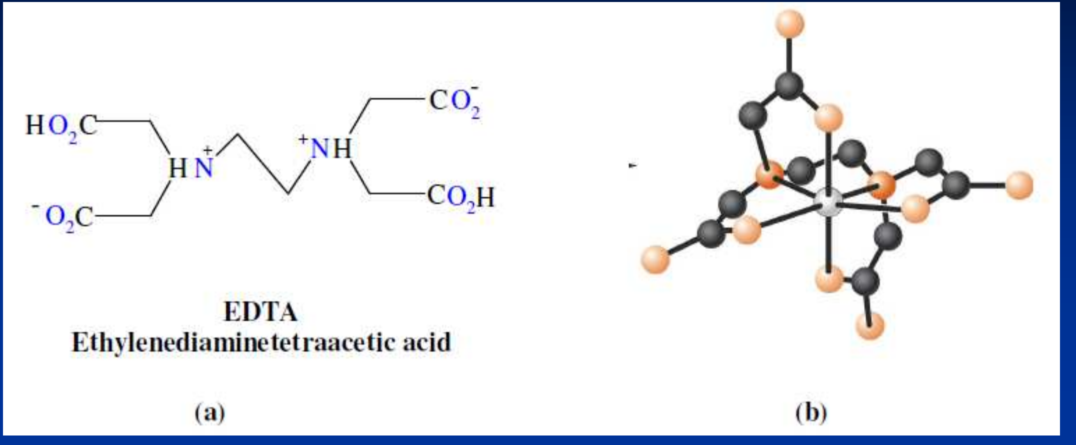
Validation parameters					
Repeatability of the method	**0,12%**	Ref. mass conecntration	**1000,0**	[mg/l]
Recovery (rel.)	**100,16%**	U, k=2	**2,0**	[mg/l]
Recovery uncertainty (rel.)	**0,11%**	u	**1,0**	[mg/l]
γ(average) - γ(ref.)	**1,6**	[mg/l]	Metrological compatibility [mg/l]	
u (γ(average) - γ(ref.))	**1,13**	[mg/l]	γ(average) - γ(ref.)	U (γ(average) - γ(ref.))
U (γ(average) - γ(ref.))	**2,27**	[mg/l]	**1,6**	**2,3**

Bismut standard solution in 2% (v/v) nitric acid

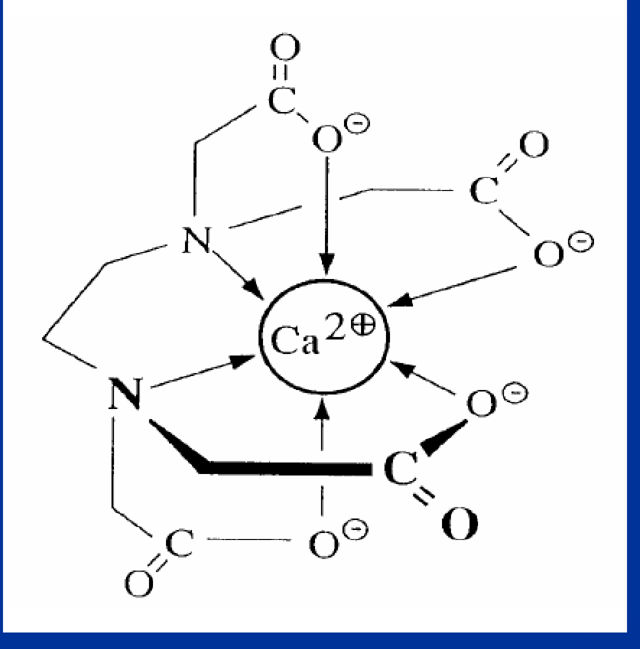
Bismut standard solution in 2% (v/v) nitric acid	Lead for the standard solution preparation weight	Lead for the standard solution preparation purity	Lead molar mass	Volume of the lead standard solution	Volume of the lead standard for the EDTA concentration determination	Volume of EDTA volumetric solution for its concentration determination	Repeatability of the EDTA concentration determination	Volume of the sample analysed (bismut stdandard solution)	Volume of EDTA volumetric solution during the titration	Bismut molar mass	Repeatability of the analysis
	a [g]	**P [1]**	**b [g/mol]**	**c [ml]**	**d [ml]**	**e [ml]**	**repeatability EDTA**	**f [ml]**	**g [ml]**	**h [g/mol]**	**repeatability**
Value	2,07888	1	207,200	1000	30,02	30,18	1	49,96	23,94	208,980400	1
Uncertainty	0,00007	0,000006	0,058	0,1915	0,0022	0,0062	0,000271	0,0017	0,0062	0,000006	0,000278
a	2,07895	2,07888	2,07888	2,07888	2,07888	2,07888	2,07888	2,07888	2,07888	2,07888	2,07888
P	1	1,000006	1	1	1	1	1	1	1	1	1
b	207,2	207,2	207,258	207,2	207,2	207,2	207,2	207,2	207,2	207,2	207,2
c	1000	1000	1000	1000,1915	1000	1000	1000	1000	1000	1000	1000
d	30,02	30,02	30,02	30,02	30,0222	30,02	30,02	30,02	30,02	30,02	30,02
e	30,18	30,18	30,18	30,18	30,18	30,1862	30,18	30,18	30,18	30,18	30,18
repeatability EDTA	1	1	1	1	1	1	1,000271	1	1	1	1
f	49,96	49,96	49,96	49,96	49,96	49,96	49,96	49,9617	49,96	49,96	49,96
g	23,94	23,94	23,94	23,94	23,94	23,94	23,94	23,94	23,9462	23,94	23,94
h	208,9804	208,9804	208,9804	208,9804	208,9804	208,9804	208,9804	208,9804	208,9804	208,980406	208,9804
repeatability	1	1	1	1	1	1	1	1	1	1	1,000278
Mass conc. (γ(u)), [mg/l]	999,43	999,40	999,12	999,21	999,47	999,19	999,67	999,36	999,66	999,40	999,68
γ(average) - γ(u), [mg/l]	-0,0337	-0,0058	0,2784	0,1913	-0,0716	0,2053	-0,2705	0,0334	-0,2588	0,0000	-0,2783
(γ(av.) - γ(u))2, [mg/l]2	0,0011	0,0000	0,0775	0,0366	0,0051	0,0421	0,0732	0,0011	0,0670	0,0000	0,0775
Contribution to the total u	**0,3%**	**0,0%**	**20,3%**	**9,6%**	**1,3%**	**11,1%**	**19,2%**	**0,3%**	**17,6%**	**0,0%**	**20,3%**
Σ(γ(av.) - γ(u))2, [mg/l]2	0,381										**100,00%**
Total uncertainty u, [mg/l]	**0,6**	Average mass concentration		999,4	[mg/l]						
U (k=2), [mg/l]	**1,2**		U (k=2)	1,2	[mg/l]						

Repeatability of the method	**0,09%**	Ref. mass conecntration	**1000,0**	[mg/l]
Recovery (rel.)	**99,94%**	U (k=2)	**2,0**	[mg/l]
Recovery uncertainty (rel.)	**0,12%**	u	**1,0**	[mg/l]
γ(average) - γ(ref.)	**0,6**	[mg/l]	Metrological compatibility [mg/l]	
u (γ(average) - γ(ref.))	**1,175**	[mg/l]	γ(average) - γ(ref.)	U (γ(average) - γ(ref.))
U (γ(average) - γ(ref.))	**2,351**	[mg/l]	**0,6**	**2,4**

Chelatometric (complexometric) determinations



(a) Structure of EDTA and (b) its metal complex

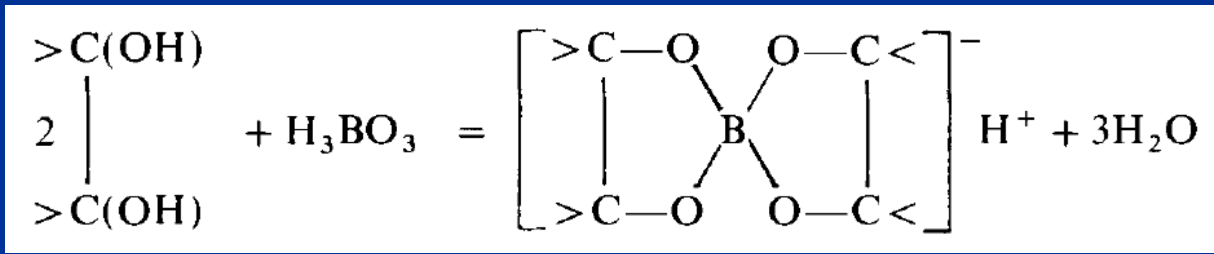


Chelatometric (complexometric) determinations
Huge amount of single element calibration solutions

No.	Analyte	γ(ref) ± U $[mg.l^{-1}]$	γ(det) ± U $[mg.l^{-1}]$	No.	Analyte	γ(ref) ± U $[mg.l^{-1}]$	γ(det) ± U $[mg.l^{-1}]$
1	Al	1000.0 ± 2.0	998.4 ± 2.0	30	Mg	1000.0 ± 2.0	1001.3 ± 1.4
2	Al	10005.0 ± 20.0	10014.8 ± 20.2	31	Mg	10003.0 ± 20.0	10005.1 ± 15.0
7	Bi	1000.0 ± 2.0	999.4 ± 1.2	32	Mn	1000.0 ± 2.0	999.0 ± 1.1
8	Bi	10000.0 ± 20.0	10016.1 ± 14.6	37	Ni	1000.0 ± 2.0	1001.0 ± 1.0
10	Ca	1000.0 ± 2.0	999.4 ± 1.2	40	Pb	1000.0 ± 2.0	1000.1 ± 1.3
11	Ca	$\boxed{10.025 \pm 0.017^{*}}$	$\boxed{10.023 \pm 0.014^{*}}$	45	Sc	1000.0 ± 2.0	999.3 ± 1.0
12	Cd	1000.0 ± 2.0	998.6 ± 1.0	46	Sn	1000.0 ± 2.0	998.2 ± 1.4
13	Cd	$\boxed{10.005 \pm 0.019^{*}}$	$\boxed{9.998 \pm 0.013^{*}}$	47	Sn	1000.0 ± 2.0	1001.8 ± 1.9
16	Co	1000.0 ± 2.0	1000.1 ± 0.9	52	Tl	1000.0 ± 2.0	998.4 ± 1.2
18	Cu	1000.0 ± 2.0	999.1 ± 1.1	53	V	1000.0 ± 2.0	1000.8 ± 5.4
19	Cu	10012.0 ± 20.0	10014.1 ± 12.0	56	Y	1000.0 ± 2.0	1001.2 ± 1.0
20	F^-	1000.0 ± 2.0	1001.1 ± 2.4	57	Zn	1000.0 ± 2.0	1001.0 ± 1.1
21	F^-	1001.0 ± 2.0	1000.6 ± 2.1	58	Zn	10013.0 ± 20.0	9998.5 ± 11.4
22	Fe	1000.0 ± 2.0	1000.5 ± 1.8	59	Zr	1000.0 ± 2.0	1001.1 ± 1.5
24	Ga	1000.0 ± 2.0	999.2 ± 1.9	60	Zr	1000.0 ± 2.0	999.6 ± 1.5
25	Hf	10000.0 ± 20.0	10023.1 ± 15.2	61	Zr	10000.0 ± 30.0	10014.0 ± 14.4
26	In	1000.0 ± 2.0	998.1 ± 1.3	chelatometric (complexometric) determination; *[mg/g]			

Other titrimetric determinations
Alkalimetry, argentometry, manganometry, bromatometry

No	Analyte	γ(ref) ± U [mg.l^{-1}]	γ(det) ± U [mg.l^{-1}]	RSD [%]	R ± u(R) [%]	Δ < U(Δ) [mg.l^{-1}]
4	B	1000.0 ± 2.0	1000.8 ± 1.1	0.05	100.08 ± 0.11	0.8 < 2.3
5	B	1000.0 ± 2.0	998.1 ± 1.2	0.08	99.81 ± 0.12	1.9 < 2.4



pK$_A$ (free boric acid) = **9.3**

pK$_A$ (boric acid-mannitol) = **5.2**

No	Analyte	γ(ref) ± U [mg.l^{-1}]	γ(det) ± U [mg.l^{-1}]	RSD [%]	R ± u(R) [%]	Δ < U(Δ) [mg.l^{-1}]
9	Br^-	1000.0 ± 2.0	1001.9 ± 1.1	0.09	100.19 ± 0.11	1.9 < 2.3
14	Cl^-	1000.0 ± 2.0	998.2 ± 1.1	0.07	99.82 ± 0.12	1.8 < 2.3
15	Cl^-	1000.0 ± 5.0	1001.0 ± 1.4	0.08	100.10 ± 0.26	1.0 < 5.2

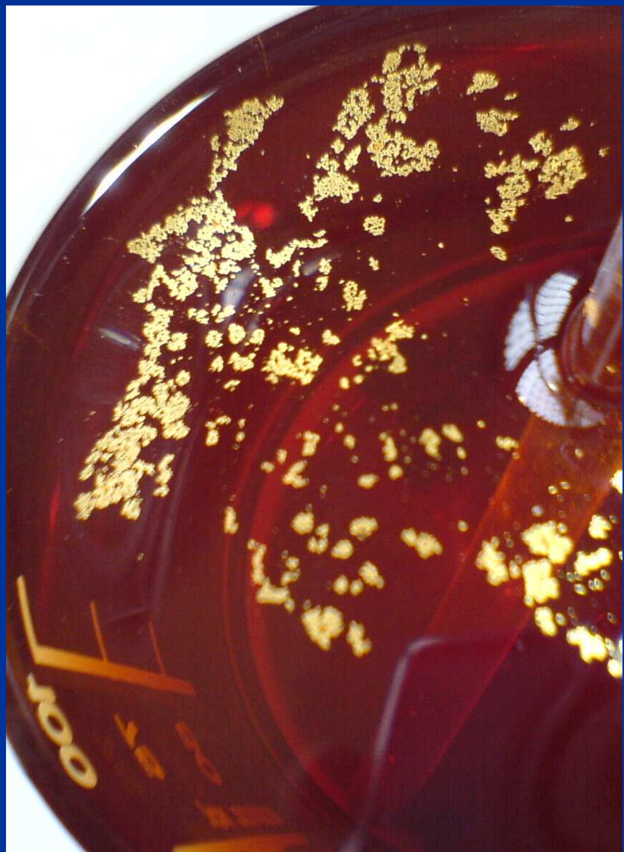
No	Analyte	γ(ref) ± U [mg.l^{-1}]	γ(det) ± U [mg.l^{-1}]	RSD [%]	R ± u(R) [%]	Δ < U(Δ) [mg.l^{-1}]
23	Fe	1000.0 ± 2.0	998.4 ± 0.9	0.07	99.84 ± 0.11	1.6 < 2.2
44	Sb	1000.0 ± 2.0	1001.6 ± 1.1	0.12	100.16 ± 0.11	1.6 < 2.3

Alkali metals calibration solutions
Determination in the form of alkali metal sulfates

No	Analyte	γ(ref) ± U [mg.l^{-1}]	γ(det) ± U [mg.l^{-1}]	RSD [%]	R ± u(R) [%]	Δ < U(Δ) [mg.l^{-1}]
29	Li	10000.0 ± 20.0	9980.9 ± 7.7	0.09	99.81 ± 0.11	19.1 < 21.4
33	Na	10000.0 ± 20.0	9991.6 ± 9.4	0.13	99.92 ± 0.11	8.4 < 22.1
34	Na	10000.0 ± 20.0	9996.6 ± 9.2	0.12	99.97 ± 0.11	3.4 < 22.0
27	K	10000.0 ± 20.0	9999.6 ± 19.3	0.29	100.00 ± 0.14	0.4 < 27.8
28	K	10000.0 ± 20.0	10012.9 ± 7.8	0.06	100.13 ± 0.11	12.9 < 21.5
42	Rb	10000.0 ± 20.0	9985.6 ± 12.1	0.10	99.86 ± 0.12	14.4 < 23.4
17	Cs	10000.0 ± 20.0	10003.9 ± 18.5	0.24	100.04 ± 0.14	3.9 < 27.2

Gold in 5% (v/v) hydrochloric acid solution
Determination using hydroquinone reduction

No	Analyte	γ(ref) ± U [mg.l^{-1}]	γ(det) ± U [mg.l^{-1}]	RSD [%]	R ± u(R) [%]	Δ < U(Δ) [mg.l^{-1}]
3	Au	1000.0 ± 2.0	999.4 ± 1.9	0.16	99.94 ± 0.14	0.6 < 2.8



Baryum in 2% (v/v) nitric acid solution
Determination in the form of baryum chromate

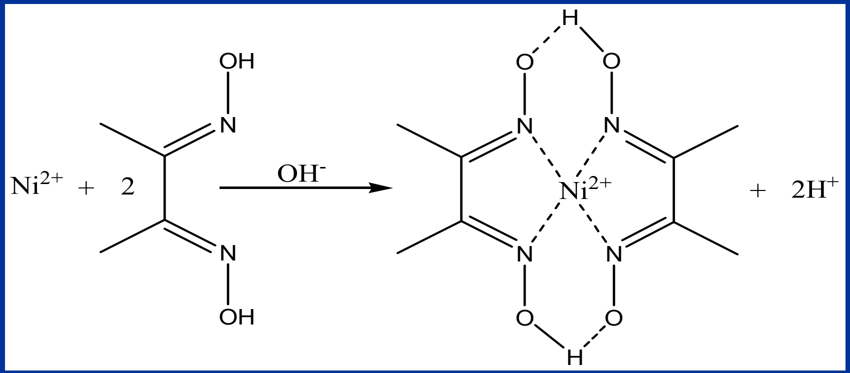
No	Analyte	$\gamma(ref) \pm U$ [$mg.l^{-1}$]	$\gamma(det) \pm U$ [$mg.l^{-1}$]	RSD [%]	$R \pm u(R)$ [%]	$\Delta < U(\Delta)$ [$mg.l^{-1}$]
6	Ba	1000.0 ± 2.0	998.5 ± 0.9	0.07	99.85 ± 0.11	$1.5 < 2.2$

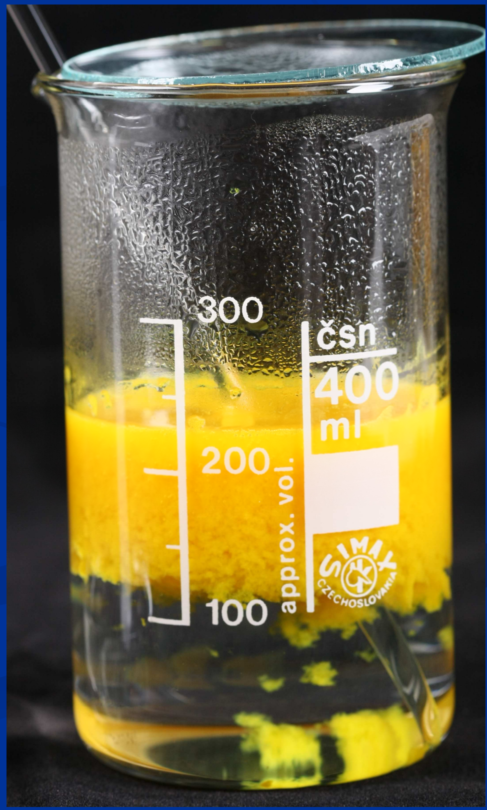
Niobium in 1% (v/v) HF and 5% HNO_3 (v/v) solution
Determination using cupferron as precipitating agent

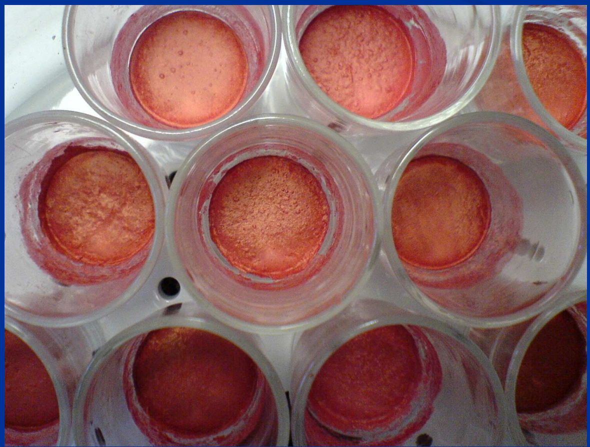
No	Analyte	γ(ref) ± U [mg.l^{-1}]	γ(det) ± U [mg.l^{-1}]	RSD [%]	R ± u(R) [%]	Δ < U(Δ) [mg.l^{-1}]
35	Nb	1000.0 ± 2.0	1000.8 ± 2.1	0.08	100.08 ± 0.14	0.8 < 2.9

Ni in 2% (v/v) HNO_3 and Pd in 5% (v/v) HCl solution
Determination using dimethylglyoxime as precipitant

No	Analyte	γ(ref) ± U [mg.l⁻¹]	γ(det) ± U [mg.l⁻¹]	RSD [%]	R ± u(R) [%]	Δ < U(Δ) [mg.l⁻¹]
36	Ni	1000.0 ± 2.0	1000.9 ± 0.9	0.08	100.09 ± 0.11	0.9 < 2.2
38	Ni	1000.0 ± 2.0	1000.8 ± 0.6	0.02	100.08 ± 0.10	0.8 < 2.1
41	Pd	1000.0 ± 2.0	998.7 ± 1.9	0.19	99.87 ± 0.14	1.3 < 2.7







Nitrate, perrhenate and wolframate in water solution
Determination using nitrone as precipitating agent

No	Analyte	$\gamma(ref) \pm U$ $[mg.l^{-1}]$	$\gamma(det) \pm U$ $[mg.l^{-1}]$	RSD [%]	$R \pm u(R)$ [%]	$\Delta < U(\Delta)$ $[mg.l^{-1}]$
39	NO_3^-	1000.0 ± 2.0	1001.1 ± 1.4	0.19	100.11 ± 0.12	1.1 < 2.4
43	Re	1000.0 ± 2.0	999.3 ± 1.4	0.14	99.93 ± 0.12	0.7 < 2.5
54	W	1000.0 ± 2.0	999.0 ± 2.5	0.14	99.90 ± 0.16	1.0 < 3.2
55	W	10000.0 ± 20.0	10007.5 ± 38.3	0.34	100.07 ± 0.22	7.5 < 43.2

Ta and Ti in 1% (v/v) HF and 5% HNO_3 (v/v) solution Determination using ammonia solution hydrolysis

No	Analyte	γ(ref) ± U [mg.l^{-1}]	γ(det) ± U [mg.l^{-1}]	RSD [%]	R ± u(R) [%]	Δ < U(Δ) [mg.l^{-1}]
48	Ta	1000.0 ± 2.0	998.5 ± 1.5	0.14	99.85 ± 0.13	1.5 < 2.5
49	Ta	10000.0 ± 20.0	10002.3 ± 25.3	0.09	100.02 ± 0.16	2.3 < 32.3
50	Ti	1000.0 ± 2.0	1000.8 ± 2.1	0.17	100.08 ± 0.15	0.8 < 2.9
51	Ti	10010.0 ± 20.0	10016.5 ± 26.2	0.24	100.07 ± 0.16	6.5 < 33.0

Standard calibration solutions analysed

Analytika, spol. s r.o., Czech Republic

National Institute of Standards and Technology, USA

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Alfa Aesar GmbH, Germany

Ultra Scientific, USA

Conclusion

- primary methods (gravimetry and titrimetry) are capable for the determination of a nominal value of the analyte mass concentration with acceptable uncertainty below 0,2% (rel.)
- metrological compatibility between analyte mass concentration value found and certified was for more than 60 solutions fulfilled

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