Precision determination of precious metals with ICP-OES

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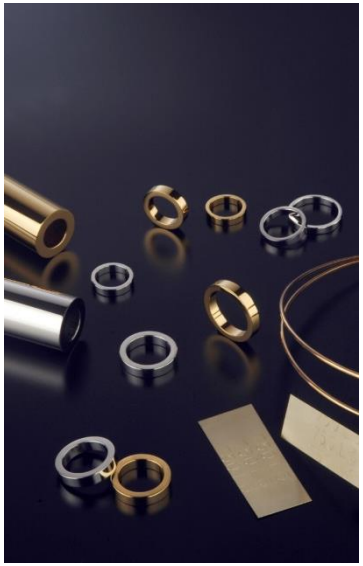
Bracketing

- **Procedure described in ISO 11494 and ISO 11495**
- **Serves to increase the precision and accuracy of the analysis results**
- **Samples are measured between the bracket standards**
- **An internal standard is used for correction**



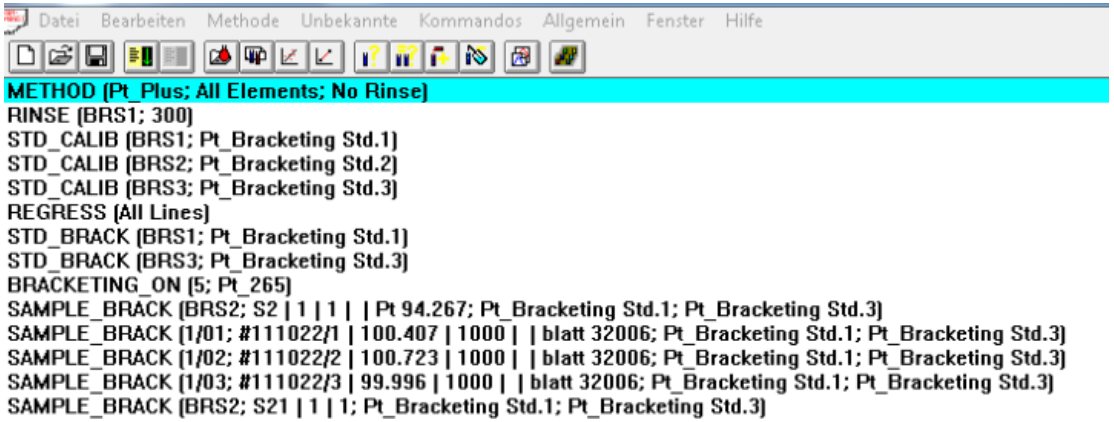
Scope ISO 11494

This document describes an analytical procedure for the determination of platinum in platinum alloys with a nominal content up to 990 ‰ (parts per thousand), including alloys according to ISO 9202.

Principle

At least two accurately weighed samples are dissolved in aqua regia and made up to an exactly weighed mass. These sample solutions are mixed with the internal standard and made up to the standard measuring volume. Using ICP-OES, the platinum content of the sample solution is measured by comparison of the ratio intensities of the spectral emission of platinum and appropriate yttrium line(s) with the ratios for solutions containing known masses of platinum and yttrium using the bracketing method.

1	low-standard	→	
2	sample		Bracket1
3	high-standard	→	
4	sample		Bracket2
5	low-standard	→	
6	sample		Bracket3
7	high-standard	→	
8	sample		Bracket4
9	low-standard	→	
10	sample		Bracket5
11	high-standard	→	



Calculation - Bracketing

$$m_{Pt} = a + \frac{(b-a)\cdot(Q_{Cs} - Q_{Ca})}{(Q_{Cb} - Q_{Ca})}$$

a	is the mass of platinum in the calibration solution used as “low-standard”, in milligrams
b	is the mass of platinum in the calibration solution used as “high-standard”, in milligrams
QCa	is the corrected intensity ratio IPt/IY of the “low-standard
Q_{Cb}	is the corrected intensity ratio IPt/IY of the “high-standard”;
Q_{Cs}	is the corrected intensity ratio IPt/IY of the sample measuring solution.

ISO 9202 - Fineness of precious metal alloys

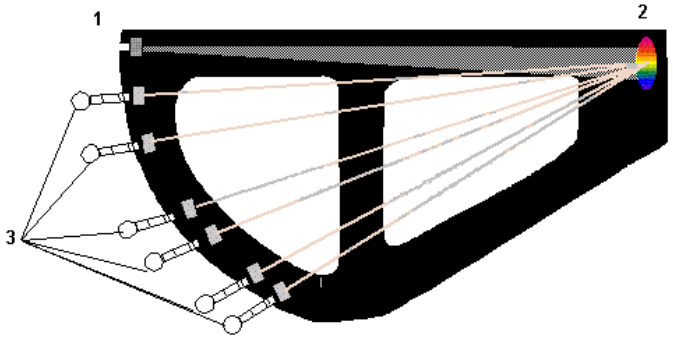
Precious metal	Fineness min	Recommended method
Au	333 - 990	ISO 11426
	999	ISO 11426 or ISO 15093
Pt	850 - 990	ISO 11210
		ISO 11494
	999	ISO 15093
Pd	500 - 990	ISO 11490
		ISO 11495
	999	ISO 15093
Ag	800 - 990	ISO 11427
		ISO 13756
	999	ISO 15096

Requirements for bracketing analysis

- ✓ ICP OES spectrometer – with radial view
- ✓ Suitable test environment
- ✓ Well educated and trained staff
- ✓ Homogeneous and representative sample

Start ISO - 11494 – 1992 First generation - ICP-OES with PM technology

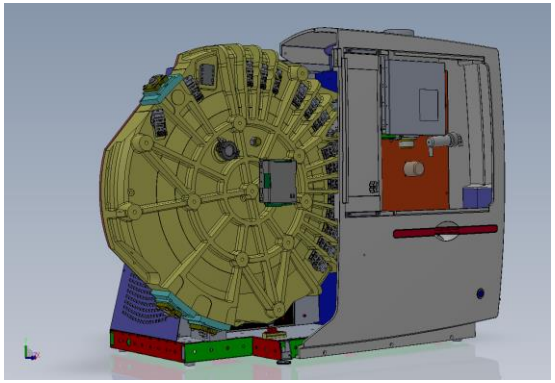
The devices had to be configured to the requirements profile demanded of the laboratory when they were ordered. Retrofitting to other spectral lines or elements was time-consuming and very expensive. In 1995, the acquisition costs for an ICP-OES with PM technology were between 130000 € and 200000 €. The requirements for the ICP devices were narrowly specified and the addition and concentration of the internal standard was defined.

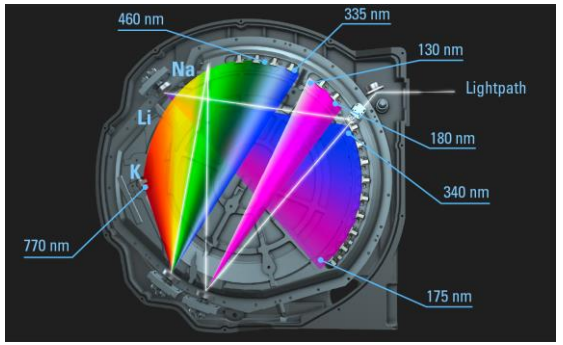


1. Eintrittsspalt 2. Gitter 3. Autrittsspalte mit Photomultiplier

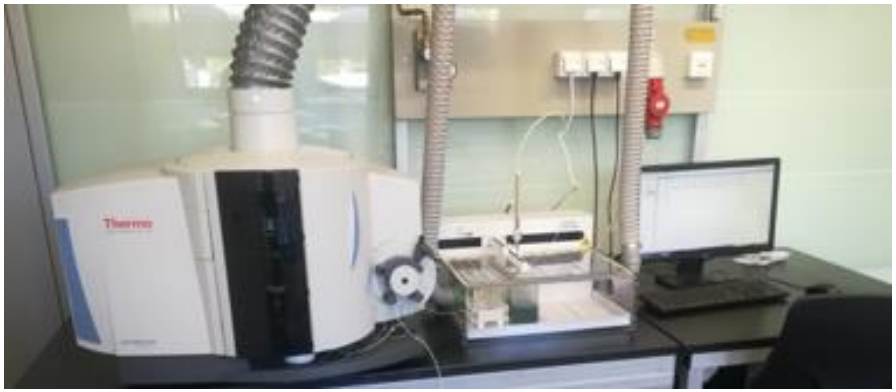
Status Quo ISO 11494:2019 ICP-OES with Chip Detection

The ICP-OES spectrometers on the market mainly use different kind of chips for the detection. Different optical systems are also used to separate the light into its spectral components. Due to the chip technology used, ICP-OES spectrometers have significantly more usable spectral lines. The price for an ICP-OES currently range between 60000 € and 80000 €.





Thermo – ICAP – 6000 – 7000 series



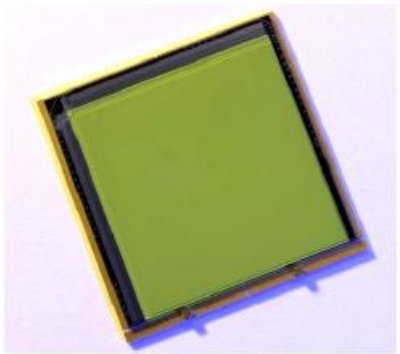


Abbildung 3: Der CID86-Detektor

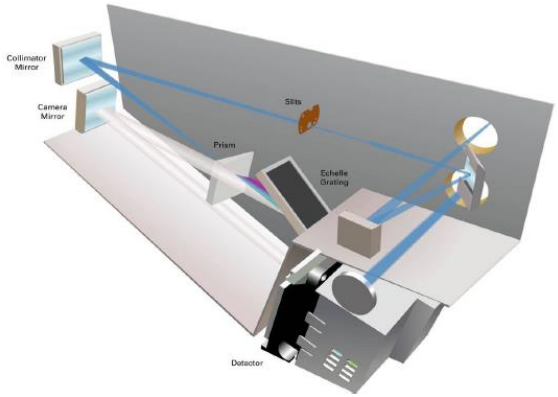


Abbildung 2: Schematische Darstellung der Voroptik zur Selektion der Plasmabetrachtung und der Echelle-Optik

Environmental conditions for bracketing measurement

1) Stable exhaust system

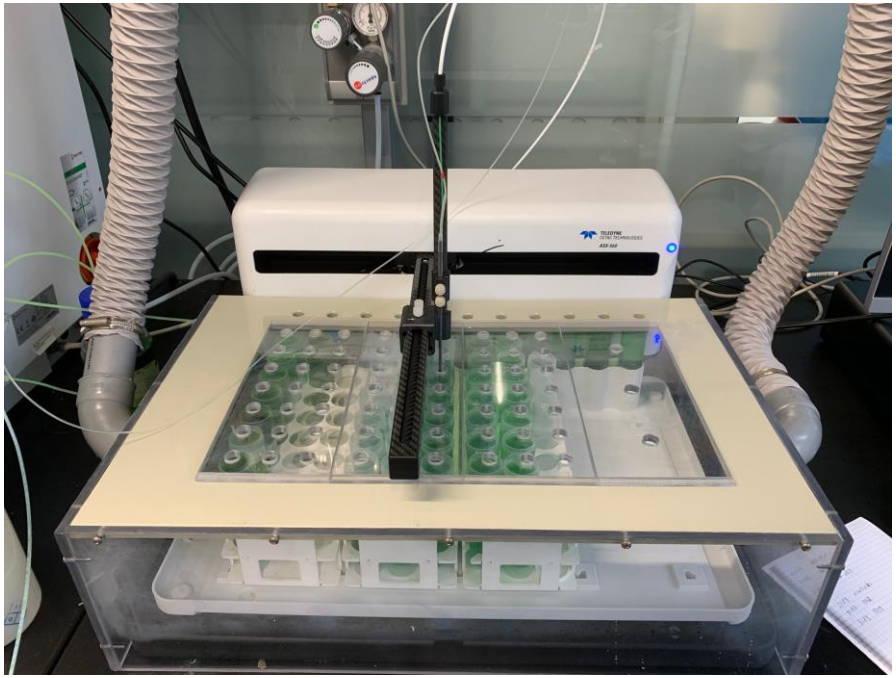
2) Draught-free supply air system

3) Sufficient air conditioning

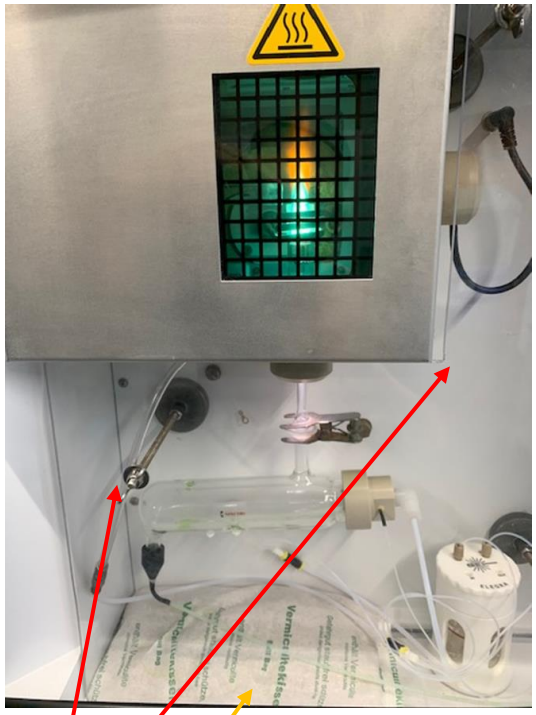
Ambient conditions for bracketing measurement

Protection against corrosion

Due to the use of up to 50 percent hydrochloric acid by volume, the measuring solutions are very corrosive. Suitable protection of the auto sampler and the sample introduction system is necessary.



Protective measures in the sample introduction system area



Plastic protective shield
Verniculite cushion

Why do we use the bracketing method for the Pt- jewellery alloys?

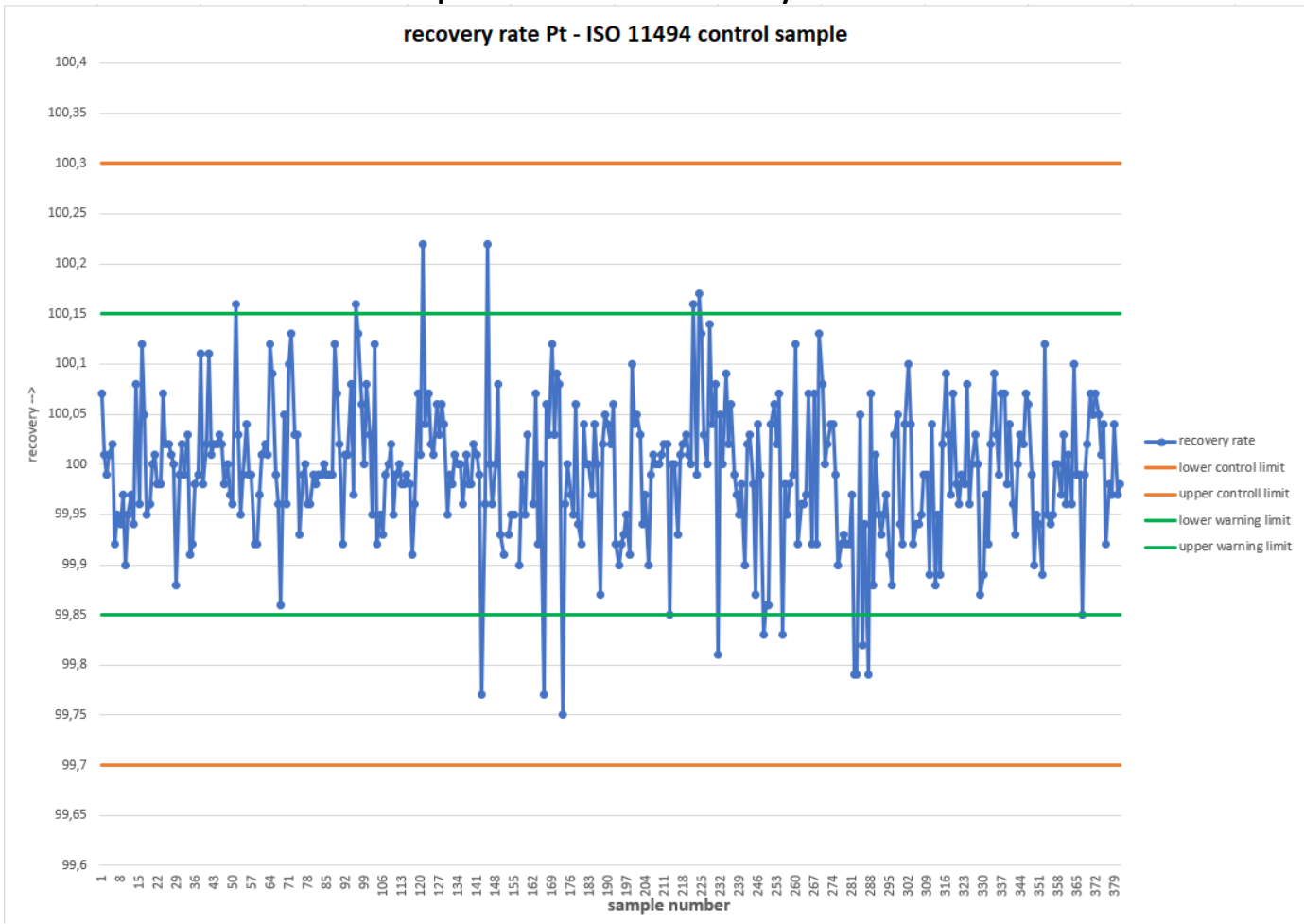
The great advantage of the bracketing method according to ISO 11494 over the gravimetric platinum determination according to ISO 11210 is that with bracketing, the other alloy metals can be analysed during the analysis and the determination can be carried out more quickly.

Determination - Pt - Bracketing ISO 11494

			Analyse in g/kg																
Lab Code	Melt ID	Bezeichnung	Pt	Pt	Ø Pt	Au		Ga		Pd		Fe		Ru	Si in g/t		C in ppm	O2 in ppm	Total
339058	3090971001	PtRu953	954,5	954,9	954,70	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,05	<0,05	45,5	45,5	<50	<50	<20	8	1000,2

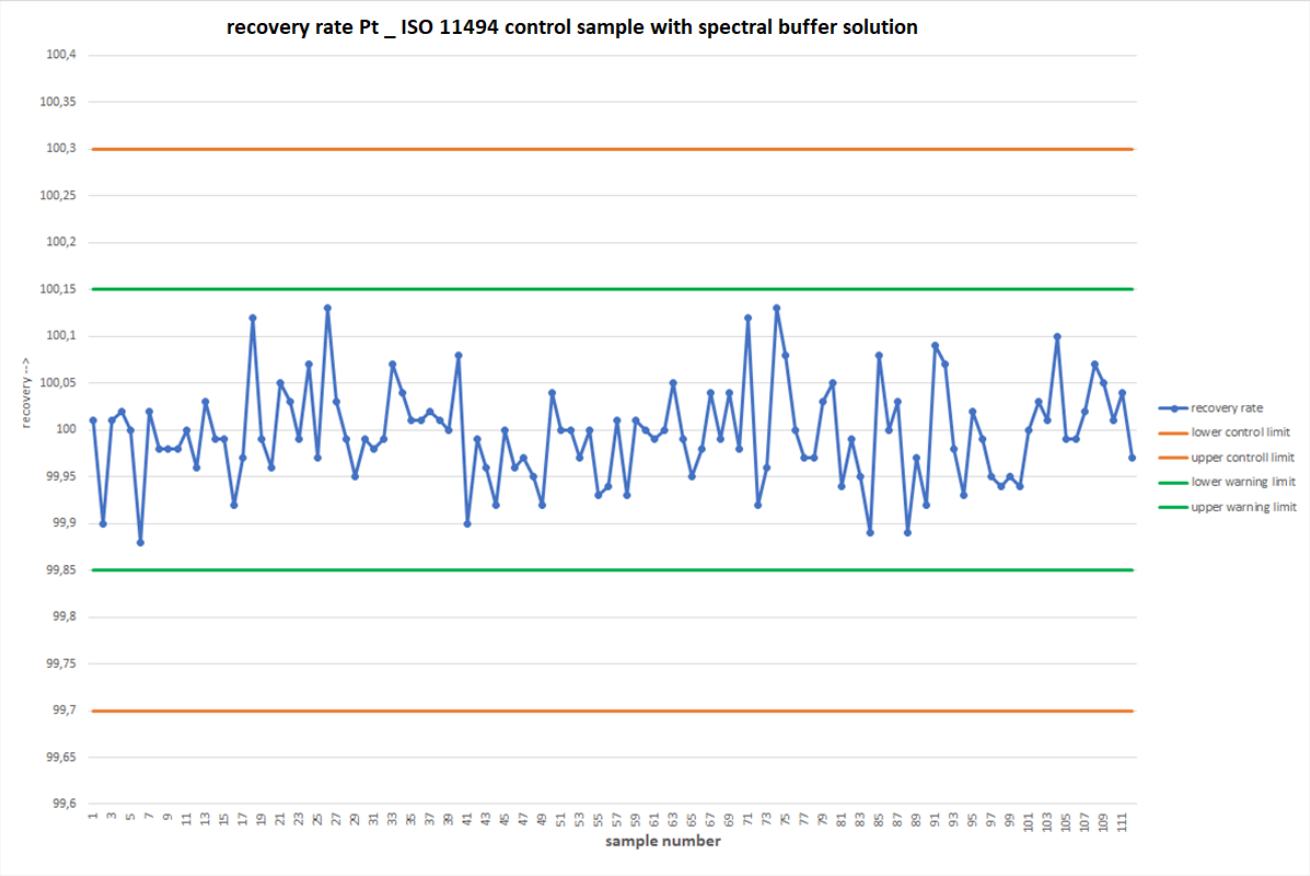
Determination of platinum and ruthenium together

Consideration of the expanded uncertainty of measurement - ISO 11494



Epanded Uncertainty Ucs
UCS = 2* Uc = 0,13 %
Uc= combined uncerainty

Consideration of the expanded uncertainty of measurement - ISO 11494

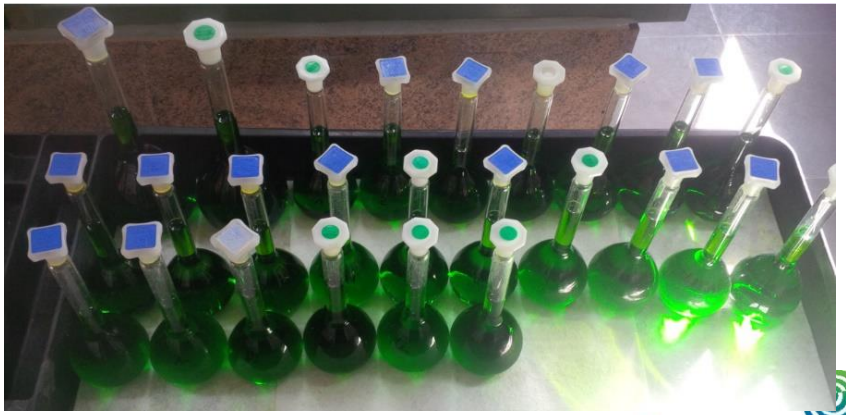


Epanded Uncertainty Ucs
UCS = 2* Uc = 0,10 %
Uc= combined uncerainty

Spectral buffer solution

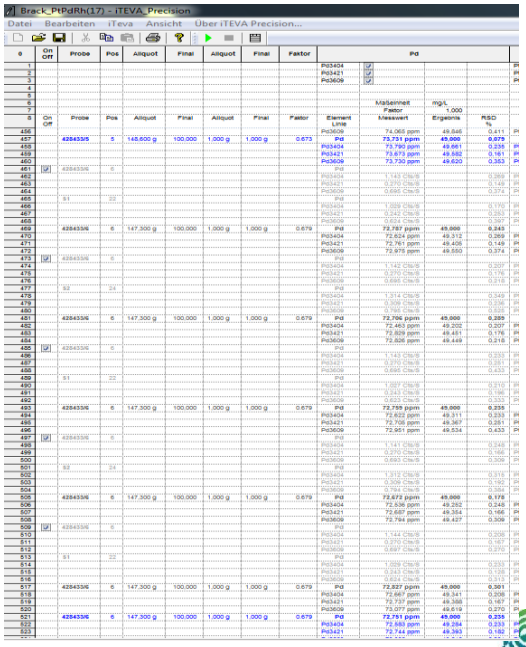
268.3 g $CuCl_2*2H_20$
37.0 g $NaNO_3$
are dissolved and made up to 1000 ml.
Add 10% by volume to the sample to be measured.
To compensate for spectral background effects and ionisation influences in the plasma.

The use of the buffer solution was provided for in the first version of ISO 11494. In subsequent revisions, the addition of the buffer was removed from the standard. In the course of the consideration of the measurement uncertainties required by ISO 17025, we found a significant improvement for our measurement uncertainty when using the spectral buffer solution.



Use of the bracketing method for analyses in precious metal refining

In contrast to jewellery alloys, where in most cases the precious metal is the main component, several precious metals are usually present in different concentrations in the refining sector. This requires a preliminary determination for the analysis in order to know the approximate concentrations of the precious metals.



As a rule, the following methods are used for digestion

Open acid digestion

Microwave digestion

Fusion digestion

1) Copper, lead or tin collection

2) Sodium peroxide digestion

3) Nickel sulphide melt

Chemicals for the Bracketing with ICP –OES – After Copper Collection

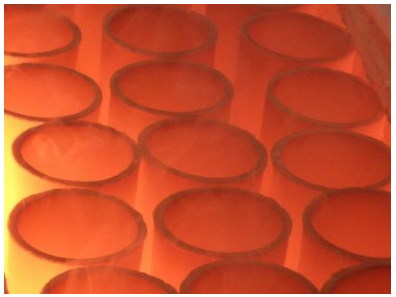
a)Hydrochloric acid

b) Nitric acid

c) Pure metals (99.99%) or weight-aliquoted solutions for the preparation of the bracketing standards.

d) Copper chloride solution and sodium nitrate solution for adjustment.

e) Internal Standard solution (Y, Sc, sometimes In)



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Comparison of ICP spectrometer with a synthetic Pt solution (99.928 g/kg)

PM-ICP				CCD - ICP - Spectro Arcos 2012				CID - Thermo ICAP 7600		
Sample	Pt_265	Pt_306		Probe	Pt 265,945	Pt 306,471		Probe	Pt2659	Pt3064
Unit	g/kg	g/kg			g/kg	g/kg			g/kg	g/kg
I.S	Y	Y			Sc	Y			Sc	Y
Spectral Buffer	X				X				X	
Power	1200 W				1200 W				1400 W	
Nebulizer	Cross -Flow				Cross -Flow				Cross -Flow	
Spray chamber	Scott with inner tube				Scott with inner tube				Scott with inner tube	
Average	100,05 g/kg	99,99 g/kg			99,94 g/kg	99,97 g/kg			100,03 g/kg	100,02 g/kg
sd	0,07 g/kg	0,06 g/kg			0,07 g/kg	0,10 g/kg			0,12 g/kg	0,08 g/kg
WFR [%]	100,13 %	100,07 %			100,02 %	100,05 %			100,11 %	100,10 %

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Round Robin Rh, Ir, Ru from synthetically produced solutions

Preparation of bracketing standards with weight aliquoted solutions

ICP	metal	result 1 [mg/kg]	result 2 [mg/kg]	result 3 [mg/kg]	result 4 [mg/kg]	result 5 [mg/kg]	result 6 [mg/kg]	**Average [mg/kg]**	Target value [mg/kg]	recovery rate [%]
									626,07	
Agosi Arcos (Chip)	Rh	626,79	626,35	625,61	625,34	626,40	626,17	**626,11**		**100,01**
Agosi PMT	Rh	627,98	627,57	627,50	626,22	626,89	626,62	**627,13**		**100,17**
									665,37	
Agosi Arcos (Chip)	Ir	662,33	661,71	661,33	661,09	661,62	661,43	**661,59**		**99,43**
Agosi PMT	Ir	663,67	663,80	662,24	662,07	662,38	661,91	**662,68**		**99,60**
									597,09	
Agosi Arcos (Chip)	Ru	596,51	596,16	595,54	595,71	596,06	595,76	**595,96**		**99,81**
Agosi PMT	Ru	597,70	595,40	595,01	594,96	595,76	595,12	**595,66**		**99,76**

Other uses of the bracketing procedure

BAM
in cooperation with the WG 'Copper'
of the Committee of Chemists of GDMB

ERM
European Reference Materials

CERTIFICATE OF ANALYSIS

ERM®-EB389

CuNi25			
	Certified value [1]	Uncertainty [2]	
Element	Mass fraction in %		
Cu	74.3	±	0.5
Ni	24.7	±	0.5
Fe	0.107	±	0.006
Mn	0.415	±	0.011
Zn	0.1125	±	0.0026
Zr	0.098	±	0.011
Mg	0.067	±	0.009

MEANS OF ACCEPTED DATA SETS (FOR ONE METHOD AT ONE LABORATORY, RESPECTIVELY)

Certified values
Mass fraction in % | Mass fraction in mg/kg

Line No.	Cu	Ni	Fe	Mn	Zn	Zr	Mg	Pb	Cr	Co	Ti	Sn	Bi	Sb	Cd	P
1	74.14	24.41	0.0993	0.402	0.1100	0.0950	0.0662	86.6	143.8	751	648	240.0	39.85	---	---	84.1
2	74.15	24.52	0.1007	0.407	0.1108	0.0953	0.0662	92.3	148.5	752	651	249.3	40.53	42.8	13.92	88.0
3	74.16	24.63	0.1053	0.408	0.1111	0.0954	0.0665	92.7	149.8	761	655	249.8	41.73	44.7	14.72	88.9
4	74.24	24.64	0.1058	0.409	0.1122	0.0954	0.0667	95.9	151.8	761	656	259.5	44.44	45.0	14.82	90.1
5	74.26	24.71	0.1065	0.419	0.1123	0.0957	0.0668	97.3	152.6	765	656	259.8	46.07	45.0	15.41	90.3
6	74.29	24.72	0.1067	0.420	0.1127	0.0970	0.0673	101.8	154.7	772	660	261.5	47.64	45.6	15.95	94.6
7	74.29	24.74	0.1071	0.421	0.1127	0.0992	0.0684	103.0	155.1	774	662	269.8	50.05	45.9	16.22	96.8
8	74.30	24.75	0.1073	0.422	0.1147	0.0994	0.0685	104.3	155.9	778	667	273.0		46.1	16.45	98,7
9	74.30	24.79	0.1077	0.423	0.1163	0.1007	0.0687	107.6	157.5	781	688	279.3		47.0	17.03	102.7
10	74.41	24.82	0.1087			0.1016		---	158.6	785		281.5		48.3		
11	74.45	24.82	0.1105							790				48.9		
12		24.98	0.1136													
13																

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Synthetic sample - Au 45 - Ag 845 -Pt 18 - Pd 22

Test measurements by means of a synthetic precious metal alloy using different spectral lines and measurement concentrations.

	Au			Ag			Pt			Pd		
Weight	**100 mg**	**150 mg**	**300 mg**	**100 mg**	**150 mg**	**300 mg**	**100 mg**	**150 mg**	**300 mg**	**100 mg**	**150 mg**	**300 mg**
Average [g/kg]	**45,13**	**45,15**	**45,05**	**845,00**	**845,07**	**844,76**	**17,99**	**18,06**	**18,02**	**21,91**	**21,94**	**21,94**
s [g/kg]	**0,10**	**0,06**	**0,04**	**0,60**	**0,47**	**0,90**	**0,07**	**0,07**	**0,05**	**0,08**	**0,05**	**0,06**
sr [%]	**0,22 %**	**0,12 %**	**0,10 %**	**0,07 %**	**0,06 %**	**0,11 %**	**0,37 %**	**0,39 %**	**0,25 %**	**0,38 %**	**0,22 %**	**0,26 %**
Wavelength [nm]	**242**	**242**	**242**	**338**	**338**	**546**	**265**	**265**	**265**	**360**	**360**	**360**
Measuring concentration [mg/L]	**4,5**	**6**	**12**	**85**	**130**	**260**	**1,8**	**2,7**	**5,4**	**2,2**	**3,8**	**7,6**

ICP-OES bracketing in comparison with analytical ISO methods

Precious metal	Sample components	ISO- Method	Recommended Method
Au	Ag, Cu, Zn Ni	Yes	ISO 11426
	High contents Pt, Pd, or Rh,Ir,Ru	No	ICP-OES
Pt	high single element solution	Yes	ISO 11210
	Au, Ag, Pd,Rh, Ir,Ru	Yes	ISO 11494
Pd	high single element solution	Yes	ISO 11490
	Au, Ag, Pt, Rh, Ir,Ru	Yes	ISO 11495
Ag	Cu, Zn, Ni, Sn…	Yes	ISO 11427 - ISO 13756
	Au, Pt,Pd, Fe	No	ICP-OES

Summary

- The ICP-OES bracketing method is a very important determination method in precious metal analysis. Besides the analysis of smaller contents, it is also possible to analyse the high contents.

- The bracketing method is an established procedure in many precious metal laboratories.

- High accuracy, speed and a high degree of automation characterise this method.

Thank you for your attention