Production and certification of Pd and Pt single spikes

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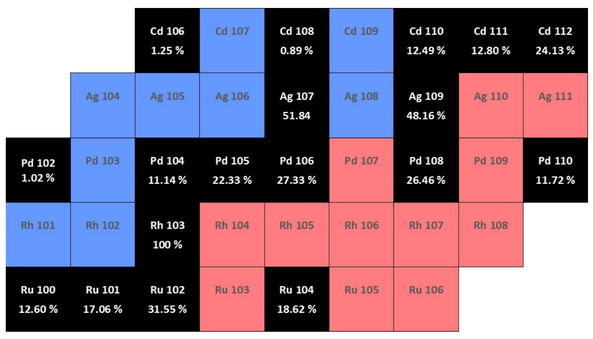
Introduction

- Isotope dilution mass spectrometry (IDMS) is considered as one of the most powerful & accurate methods for elemental analysis [1].
- IDMS is based on weighings and isotope ratio determination
- Therefore IDMS is largely unaffectedy by losses of analyte, because each subsample reflects the same isotope ratio.
- IDMS is also largely unaffected by instrumental drift, setup, matrix or sample preparation, provided blank, interferences and mass discrimination is under control.
- Considering this, IDMS is the most important reference method for elemental analysis, offering smallest measurement uncertainties.
- Due to the above described advantages IDMS often is applied for quantification of platinum group elements (PGE), either for reference material characterization or for geochemical research.

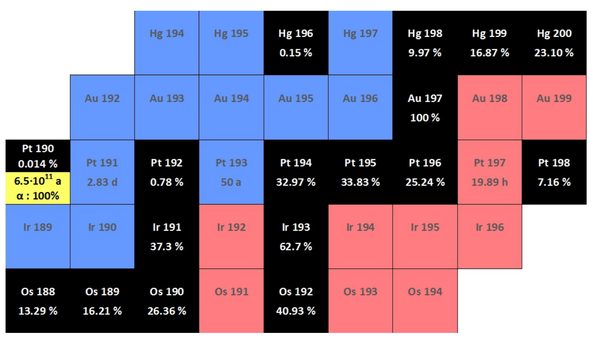
Objective

Production, characterization and certification of a ^{194}Pt and a ^{106}Pd spike solution

Selection of isotopes



- Isobaric interferences on all Pd isotopes but ^{105}Pd
- Cd and molecular interferences, e.g. $^{88}Sr^{16}O$, can be separated by ion exchange
- ^{105}Pd is natural reference isotope
- ^{106}Pd is selected as spike isotope



- Isobaric interferences on ^{190}Pt, ^{192}Pt, ^{196}Pt & ^{198}Pt
- Molecular interferences, e.g. $^{156}Gd^{40}Ar$, can be separated by ion exchange
- ^{195}Pt is natural reference isotope
- ^{194}Pt is selected as spike isotope

Preparation and ampoulation of spikes

^{106}Pd spike

- 40 mg ^{106}Pd from Oak Ridge National Laboratories
- Chemical purity > 0.9999 kg·kg^{-1}
- ^{106}Pd enrichment ~ 0.9848 mol·mol^{-1}
- Mass fractions in final solution:
  - w(HCl) = 0.20 kg·kg^{-1}
  - w(Pd) ~ 18 mg·kg^{-1}
- In precleaned quartz ampoules
- Flame sealing of ampoules

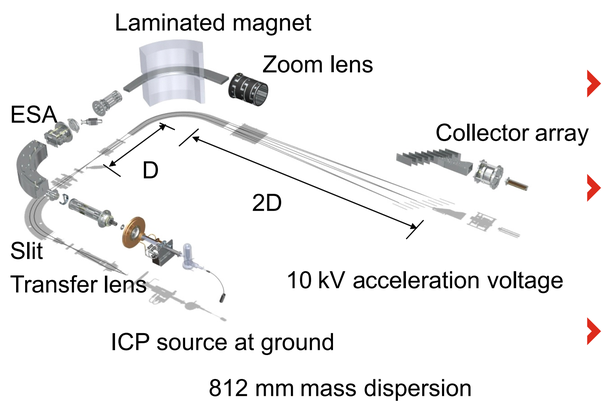
^{194}Pt spike

- 40 mg ^{194}Pt from Oak Ridge National Laboratories
- Chemical purity > 0.9999 kg·kg^{-1}
- ^{194}Pt enrichment ~ 0.9146 mol·mol^{-1}
- Mass fractions in final solution
  - w(HCl) = 0.20 kg·kg^{-1}
  - w(Pt) ~ 18 mg·kg^{-1}
- Precleaned quartz ampoules
- Flame sealing of ampoules

Preparation of back-spikes

- According to BAM quality standards two independent back-spike materials are used for spike characterizations
- Pd high purity starting material for preparing primary assays:
  - Material A offers a claimed purity of 99.99 % (Alfa Aeser)
  - Material B offers a claimed purity of 99.9 % (Heraeus)
- Pt high purity starting material for preparing primary assays:
  - Material A offers a claimed purity of 99.99 % (Alfa Aeser);
  - Material B offers a claimed purity of 99.9 % (Heraeus)
- Preparation of stock solutions under full gravimetric control

Characterization measurements



- 3 ampoules of each spike
- Each spike solution mixed twice with each back-spike
- 12 blends measured twice with a MC-ICPMS (Thermo Neptune)
- Ru, Cd and Hg have been measured simultaneously and found at background level
- Other interferences have been checked separately with a HR-ICP-MS (Thermo Element 2)
- Pd & Pt w = 200 µg·kg^{-1}

Results and Discussion

- Main observed isotope ratios: ^{105}Pd/^{106}Pd, ^{195}Pt/^{194}Pt
- „Internal“ precision (std. dev.) better than 0.005 % for blends & standards, and better than 0.05 % for spike measurements
- Reproducibility is ~ 0.005 % (back-spike, SD_{mean}, 25 h)
- Standard deviation of all blends is 0.02%, SD_{mean} is 0.006 %
- Determined ^{106}Pd mass fraction: 20.235 (16) mg·kg^{-1}
- Determined ^{194}Pt mass fraction: 18.185 (78) mg·kg^{-1}
- The isotope amount fractions are as follows:

$n(^{102}Pd)/n(Pd)$	$n(^{104}Pd)/n(Pd)$	$n(^{105}Pd)/n(Pd)$	$n(^{106}Pd)/n(Pd)$	$n(^{108}Pd)/n(Pd)$	$n(^{110}Pd)/n(Pd)$
0.00007798 (93)	0.0012287(78)	0.007408(21)	0.985429(31)	0.004717(18)	0.0011393(85)

$n(^{190}Pt)/n(Pt)$	$n(^{192}Pt)/n(Pt)$	$n(^{194}Pt)/n(Pt)$	$n(^{195}Pt)/n(Pt)$	$n(^{196}Pt)/n(Pt)$	$n(^{198}Pt)/n(Pt)$
0.00000108(51)	0.0003125(19)	0.91430(36)	0.06755(30)	0.015990(63)	0.001848(13)

Conclusion

- ^{106}Pd & ^{194}Pt spike have been successfully characterized, ERM certification procedure is running
- Measurement uncertainties are dominated by IUPAC values [2], which cancel in double IDMS; setting them constant, results in lower uncertainties: $w(^{106}Pd)$ = 20.2347 (53) mg·kg^{-1}, $w(^{194}Pt)$ = 18.1851 (51) mg·kg^{-1}
- *K*-factors for Pt were inconsistent; recalculation with exponential law results in improved isotopic composition for natural Pt

Acknowledgement

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Literature

[1] Vogl J, Pritzkow W, MAPAN – Journal of Metrology Society of India, 25 (2010) 135-164
[2] Berglund M, Wieser ME, Pure Appl. Chem. 2011, 83, 397-410.
[3] EMRP-ENV02 „PartEmission“, http://www.ptb.de/emrp/partemission.html