Potentiometric titration according to ISO 11427

Stefan Zorn – Head of Analytical Services – Agosi AG

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This presentation shows

- The influence of oxygen on the standard solution factor for the determination.
- The application of the potentiometric titration for jewellery alloys and precious metal refining
- Limiting the potentiometry by other metals and solvent residues
- Alternative methods of silver determination (ICP-OES).
- Accuracy and robustness of the potentiometric titration

Influence of oxygen in fine silver during potentiometric silver titration according to ISO 11427

The following slides shows the influence of oxygen in the determination of the titer in the potentiometric silver determination according to ISO 11427.
The oxygen content of commercially available silver granules is between 100 and 800 ppm. This oxygen content is not taken into calculation when determining the titer of the titration solution. For this reason, internal measurements were carried out here with various fine silver materials.

Simulation of the influence of oxygen by Jonathan Jodry

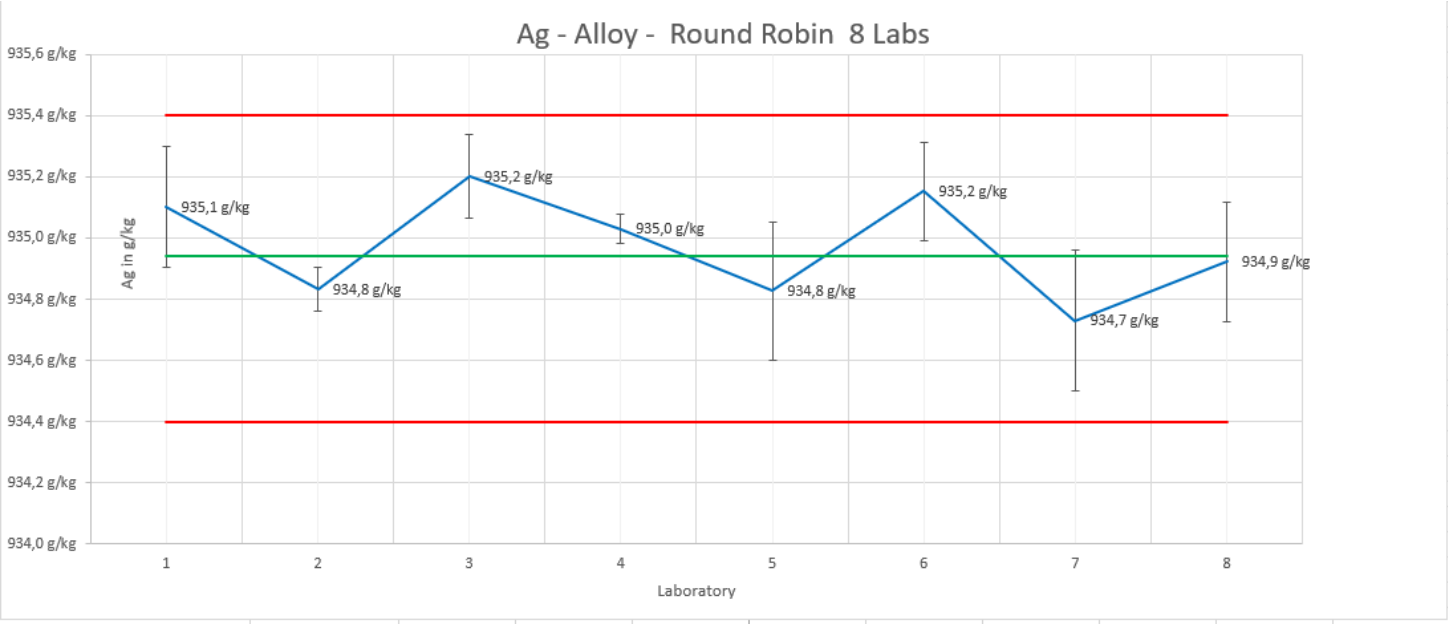
Simulation the ISO method with 3 different silver proofs :

- Case A : virtually pure silver, containing almost no oxygen
- Case B : typical silver proof containing 80 ppm of impurities and 100 ppm of oxygen (in the ISO new version spec)
- Case C, using silver grains containing lots of oxygen (400 ppm) and the same amount of impurities (out of ISO new version spec)

Simulation of the influence of oxygen by Jonathan Jodry

silver proof	**Case A**			**Case B**			**Case C**	
metallic impurities	0	ppm		80	ppm		80	ppm
oxygen	0	ppm		100	ppm		400	ppm
real Ag proof fineness =	1000,00	o/oo		999,82	o/oo		999,52	o/oo
m(AgF) =	500	mg		500	mg		500	mg
V(AgF) =	50	mL		49,991	mL		49,976	mL
F =	10			10,0018			10,0048	
sample								
weight =	500	mg		500	mg		500	mg
real fineness =	925	o/oo		925	o/oo		925	o/oo
V(Ags) =	46,25	mL		46,25	mL		46,25	mL
calculated m(Ags) =	462,5	mg		462,5833	mg		462,7221	mg
calculated fineness w(Ag) =	925	o/oo		925,1665	o/oo		925,4442	o/oo

8 different laboratories participated in this round robin test. All laboratories used the same silver (oxygen content < 20 ppm).
The mean value over all laboratories is 934.9 g Ag/kg. The variation was very small.



Internal round robin – Agosi laboratory

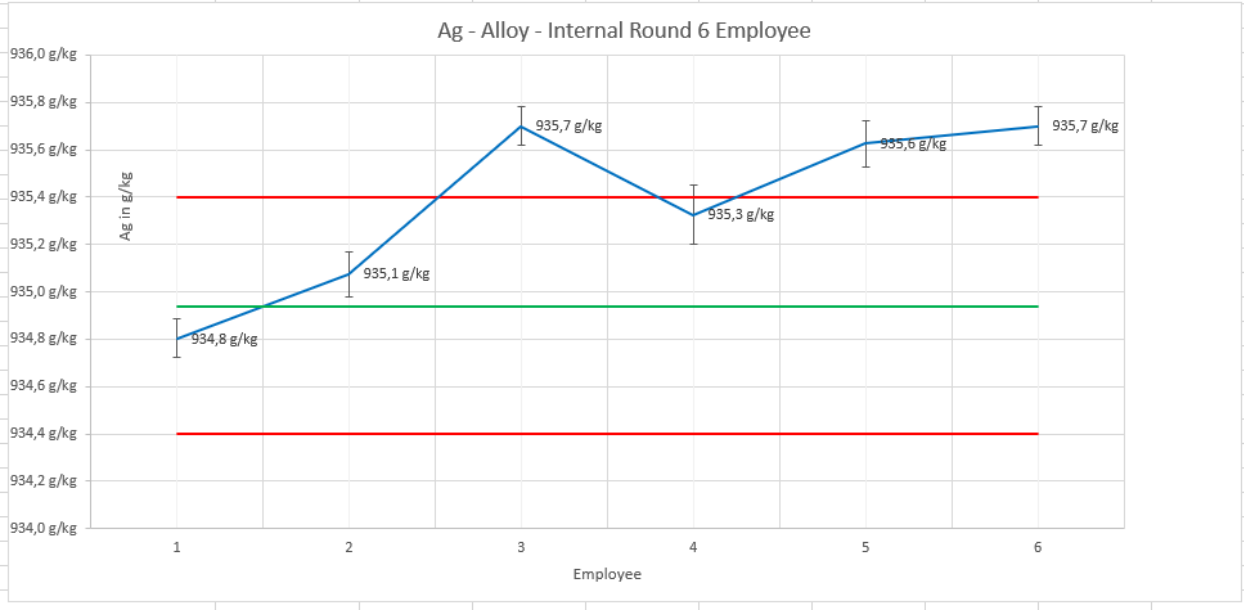
An internal round robin was carried out with the same silver alloy, in which the employees used different fine silver materials for the determination of the titer.

Employee 1-2 Silver sheet with < 20 ppm oxygen.

Employee 3-4 Silver granules with approx. 300 - 400 ppm oxygen

Employee 5-6 Silver granules with approx. 580 - 700 ppm oxygen

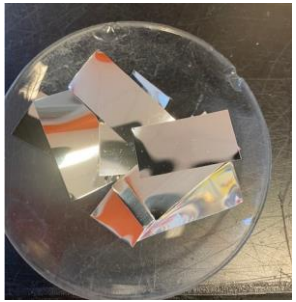
Internal round robin – Agosi laboratory



The mean value over all laboratories is 935,3 g Ag/kg.
It can be clearly seen in the results that the oxygen content in the silver, which was not taken into account, led to increased results.

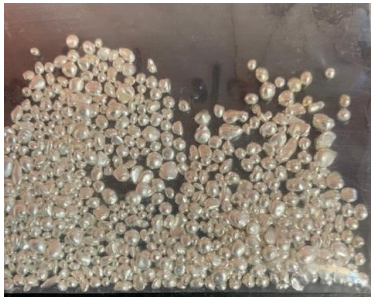
Fine silver materials used for the determination of potassium bromide factor

Titer material 1



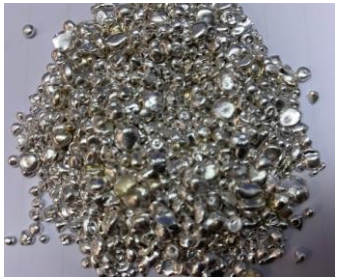
Silver sheet with
< 20 ppm oxygen

Titer material 2



Silver granules with approx.
300 - 400 ppm oxygen

Titer material 3



Silver granules with approx.
580 - 700 ppm oxygen

The two analysis comparisons clearly show the influence of the oxygen content on the determination of the silver in the potentiometric titration. With the silver granules available on the market, the oxygen content cannot be specified exactly. For this reason, wire, sheet metal or stamped pieces should be used when determining the titer of the titration solution.

Jewellery and precious metals — Determination of silver— Potentiometry using potassium bromide

1 Scope

This document specifies a volumetric method for the determination of silver on a material considered homogeneous. The silver content of the sample lies preferably between 100 and 999,0 parts per thousand (‰) by weight. Fineness above 999,0 ‰ can be determined using a spectroscopy method by difference (e.g. ISO 15096).

4 Principle

The sample is dissolved in dilute nitric acid. The silver content of the resulting solution is determined by titration with standard potassium bromide solution using a potentiometric indication of the equivalence point.

5.4 Pure silver, minimum purity 999,9 parts by mass per thousand (‰) and with an oxygen content < 100 ppm. The laboratory shall guarantee by analysis or validation that this requirement is meet.

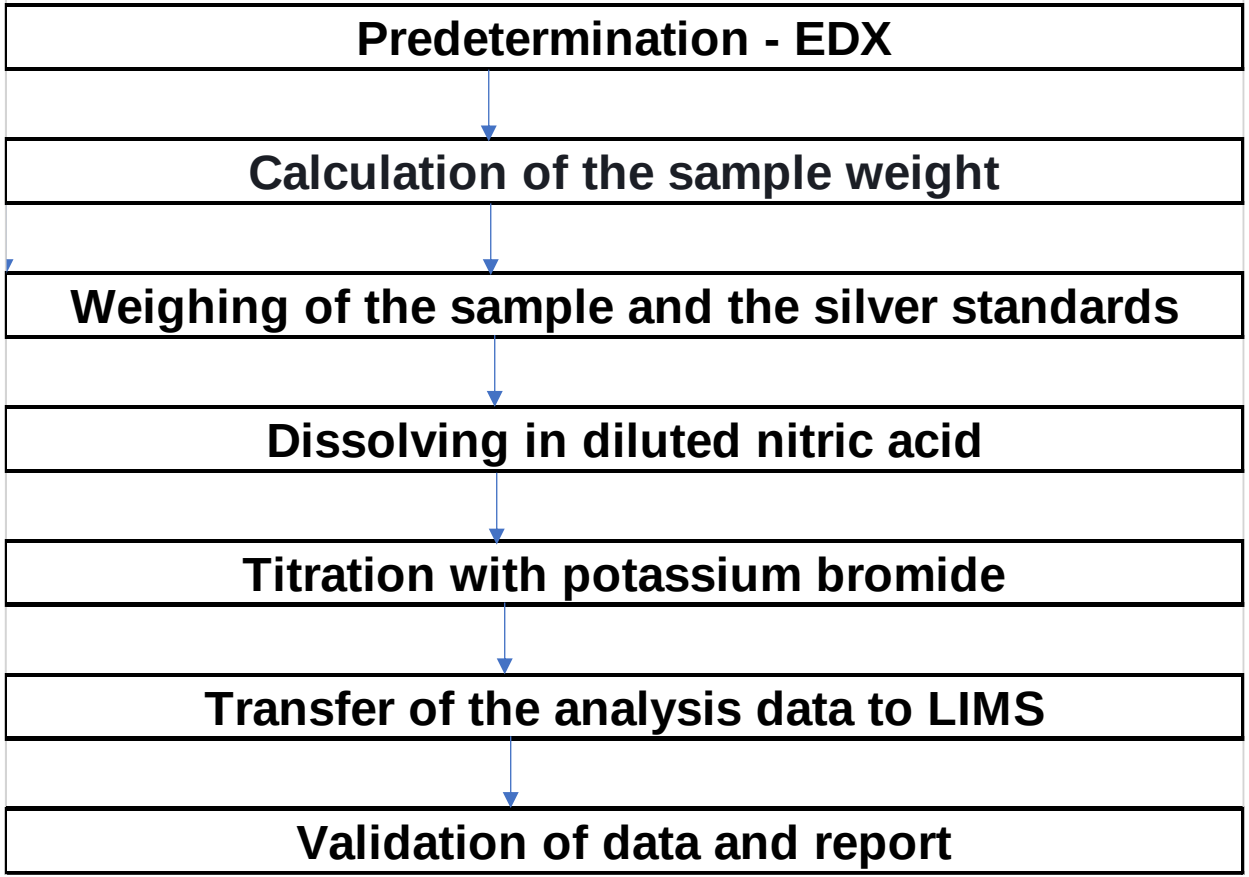
NOTE Silver sheets contain usually less than 100 ppm of oxygen.

The application of the potentiometric titration for jewellery alloys and precious metal refining

For the Agosi laboratory, potentiometric silver determination is a very important analytical method for the determination of silver for:

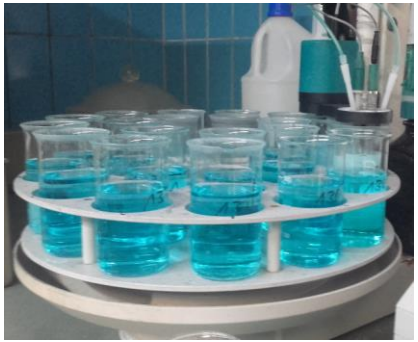
1) Direct production control for analytical control of the silver continuous casting plant.
2) Control of the silver content in the alloys produced.
3) Determination of the silver content in refining materials for settlement with the customer.

Silver titration procedure in the Agosi AG laboratory

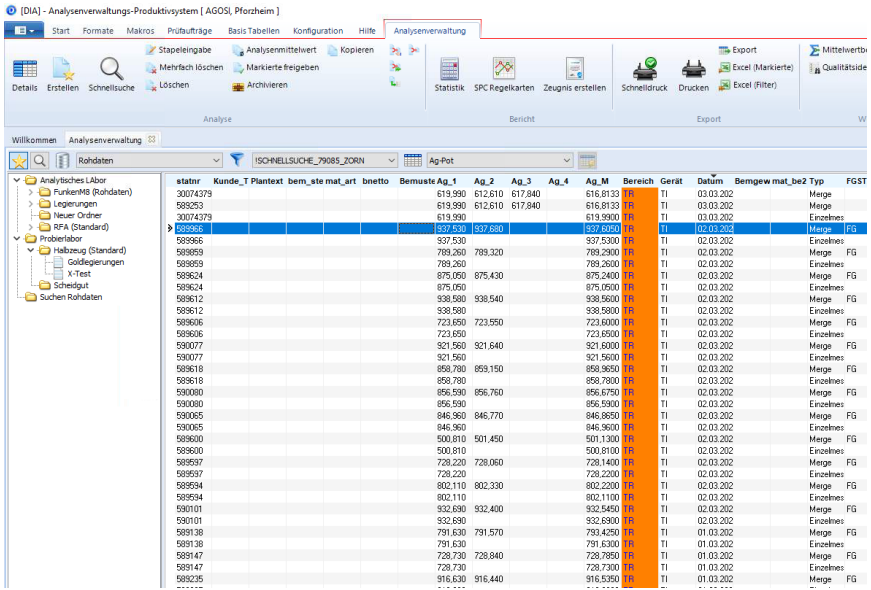


Tools and equipment for efficient work

Stamped silver pieces with different weights. Ag 99.99 % with an oxygen content of < 20 ppm oxygen



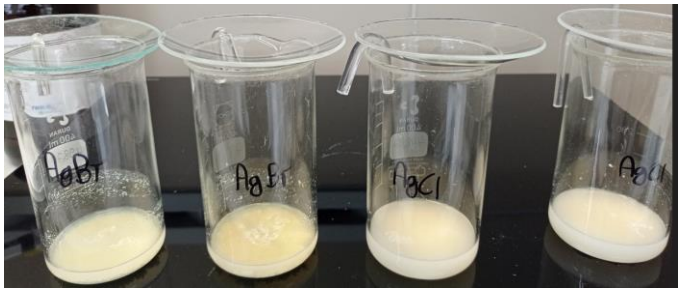
Titrator with sample changer for 400 ml beakers



LIMS system for data exchange

Limitation from insoluble silver compounds

For example, silver chloride and silver bromide. These compounds are present in many refining materials. By fuming and boiling with sulphuric acid, these compounds can be converted into silver sulphate and the solution can be titrated.



Limitation of silver determination by other metals and residues

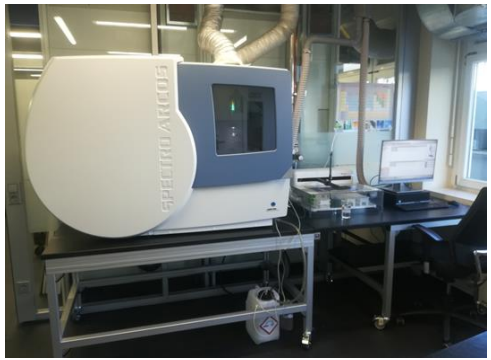
Gold, platinum and other metals prevent the silver from dissolving in nitric acid above certain concentrations. By melting with copper, a dilution is created and the silver can be dissolved and titrated. Insoluble matrix components and base metals are transferred to the slag during the copper extraction melt, so that interfering components (SiO_2, Al_2O_3, Fe...) are not present during titration.

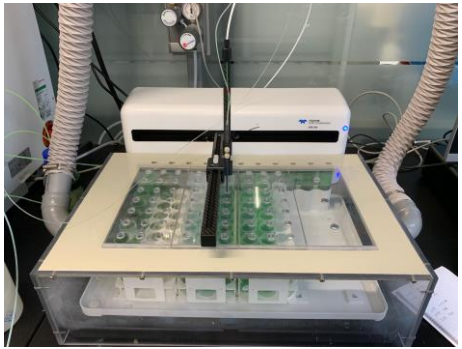

Alternative methods of silver determination (ICP-OES)

As an alternative to potentiometry, an ICP-OES method was developed.

DIN 32562:2022-08
Jewellery and precious metals - Determination of silver in silver alloys - ICP-OES method using an internal standard element

The DIN standard 32562 is to be adopted as an ISO standard. The project has started.





Principle:

The samples are first dissolved in nitric acid and then carefully precipitated with concentrated hydrochloric acid first and then dissolved again.

$Ag^+ + NO_3^- + 2HCl \rightarrow H[AgCl_2] + HNO_3$

These sample solutions are mixed with an exact amount of internal standard and made up to the measurement volume or final weight.
The bracketing method is used for this purpose.

Comparison ICP-OES - potentiometric titration

ICP-OES

Results in g/kg

Ag	Cu	Sn	Zn	total
602,0	228,9	29,3	140,2	1000,4
602,7	228,7	28,7	139,6	999,7

Titration

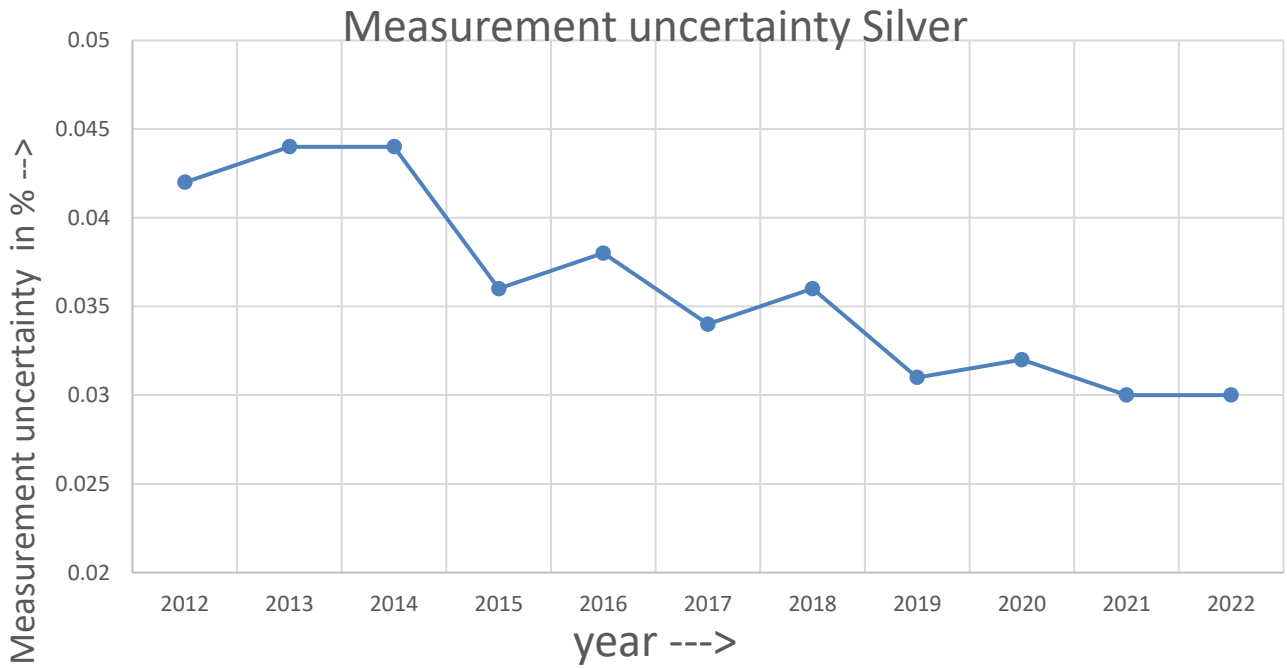
Results in g/kg

Ag
602,2
602,3

Comparison ICP-OES - potentiometric titration

	ICP-OES	Potentiometric Titration
Measurement uncertainty	0,13 %	0,05 %
Analysis time	1 day	1 hour
Elements	Multielement determination	Only silver
Sample preparation	Complex sample preparation	Simple , flexible sample preparation

Uncertainty of measurement of potentiometric silver titration over the last 10 years



Summary:

Potentiometric titration is characterized by high robustness.
The speed, accuracy and cost of the method are not reached by any other determination.

For multi-element determinations and materials that are not directly dissolvable in nitric acid, ICP -OES offers a good alternative.

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Thank you for your attention