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The golden link

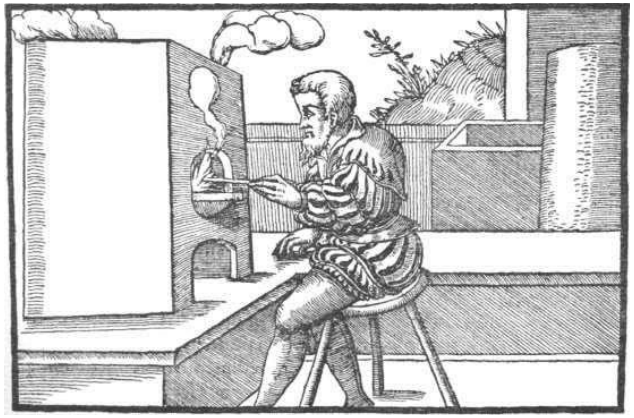
Problem Elements in Precious Metals Assaying

Alessandro Ruffoni, London, 20th March 2017

High-tech precious metals processing

Analytical needs

The practical needs of the precious metals branch have evolved



In the past gold and silver were analyzed by direct methods like cupellation.

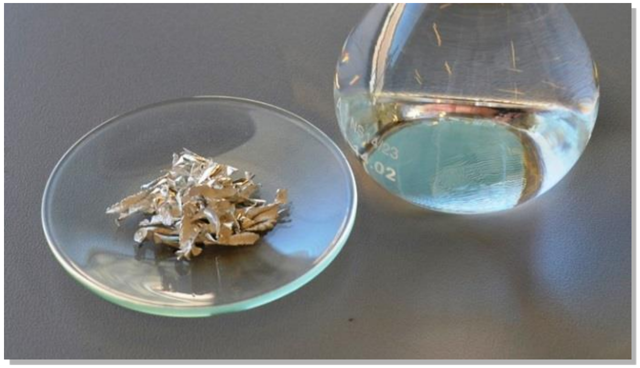
Still today these methods remain essential.

Nowadays the quest for higher purity and the need for deeper chemical characterization have opened the door to newer, highly precise and sensitive analytical techniques like spark- or inductively coupled plasma-optical emission spectroscopy, or x-ray fluorescence spectroscopy.

Analytical methods

For production control purposes laboratory devices allowing to perform the analysis on solid samples, like XRF or Spark-OES, are much preferred since the time consuming dissolution of the samples can be avoided and short lead times are thus possible.

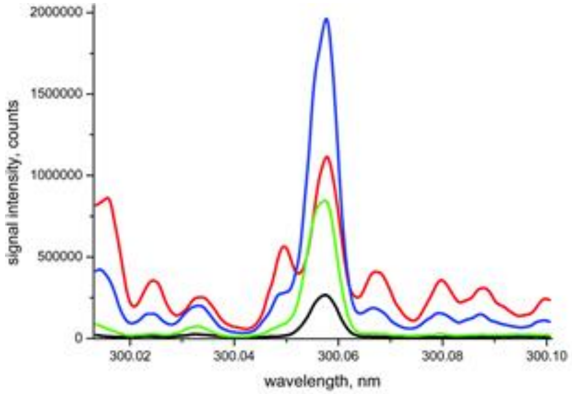
However, calibrations need to be backed up with methods allowing the required traceability to base units of mass and amount of substance.
ICP-OES, combining these requirements with a very high flexibility in its use and with affordable prices, has thus become an inescapable working tool in the precious metals assay laboratories.

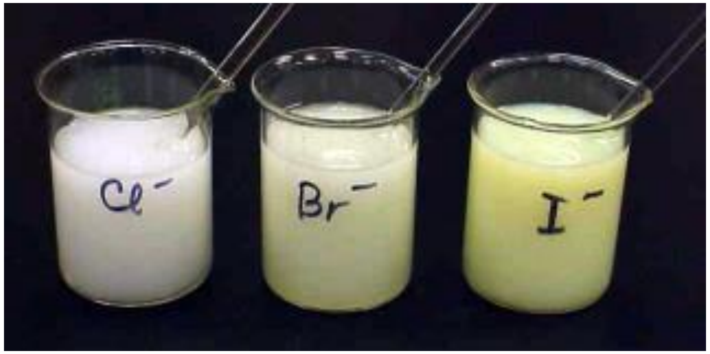


Analytical problems

When using ICP, several kinds of problems can arise, namely

- Spectrographic problems





- Chemical problems

- Methodological problems

Spectrographic problems

Spectral lines overlapping

In optical emission spectral interferences are not particularly frequent when analyzing precious metals, but sometimes arise.

- A comparison of the results derived from different emission lines is helpful, at least when developing new analytical programs and when analyzing unusual materials.
- Present-day analytical software allows multi-element calibrations and spectra deconvolution (based on the expected position and shape of the emission lines). Although scientifically well backed up, these approaches may not be sufficiently reliable when high accuracy is needed.

Weak emission lines

The nowadays much proposed axial viewing of the plasma allows higher sensitivity. When the signal-to-background ratio is unfavorable, however, miracles are not likely to happen!

Chemical problems

Insolubility and precipitation

The total dissolution of a sample is critical to ensure accurate data. Issues can originate from chemical problems, namely:

- Lack of solubility of some trace elements in the acid used to digest the matrix metal, as it happens with gold in silver.
- Reaction of the dissolved species with the solvent, like the precipitation of insoluble salts of silver and lead in hydrochloric solutions, or the formation or metastannic acid in nitric acid solutions.

Possible ways out from these situations are:

- ***<u>Pressure dissolution</u>***
  Microwave digestion units are nowadays standard in most laboratories and help to overcome many digestion problems.
  The chemistry is similar but not totally identical with the one used for the dissolution on hot plates; technical literature and suppliers application labs are helpful to define the appropriate acid mixtures and heating programs.

Chemical problems

- ***Metallurgical dilution***
  Sometimes getting the specific elements finely dispersed within the right matrix allows to overcome the solubility problems.
  This is however time consuming, and possible losses have a negative impact on the final accuracy.

- ***Recovery and separate treatment of the insoluble components***
  In some cases, as it happens for gold when silver is dissolved in nitric acid, the minor component simply remains undissolved after the digestion process.
  In this case it can be separated by appropriate means and treated separately, as shown further in this presentation.

- ***Solubilization with complexing agents***
  The use of complexing agents can help to keep specific elements in solution. A particular case is the one of silver in hydrochloric solutions, where an excess of chloride ions prevents silver from precipitating as silver chloride, keeping it in solution as silver dichloride complex ion.

Chemical problems

The fineness determination of Au 995‰ containing up to 5‰ silver by ICP, leading to inconsistent results when performed using the standard recipe (10 g/l Au and 20 ml aqua regia) becomes thus possible and reliable when the sample weight is reduced and additional hydrochloric acid is added to the working solutions.

Contamination

Despite of its chemical inertness, the glassware used for the dissolution on a hot plate releases small amounts of its components, thus compromising the accuracy of silicon and boron determination.

Although their use is not as practical as glassware, beakers and volumetric flasks made of PTFE or other plastic materials have to be used in this case.

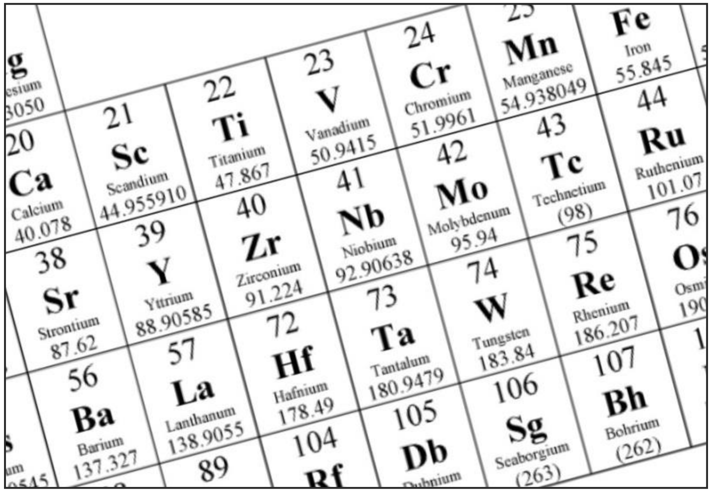
Methodological problems

Unexpected or unaccounted elements

The most problematic elements in indirect fineness determination are the ones you don’t look for.

Guidance is sometimes given, for example in the LBMA Good Delivery Rules Annex M, but it is responsibility of the assayer not to oversee elements present in the metal.

Experience and knowledge of the processes leading to the assayed material are an important prerequisite, along with crosschecks or plausibility checks with direct methods.



Analytical standards

Looking for international standards

The indirect analysis of gold and silver by trace elements determination performed by ICP is described in ISO 15093:2015 (for 999 ‰ gold) and in ISO 15096:2014 (for 999 ‰ silver).

Surprisingly at first glance, fineness grades like Au 999.9 ‰, Au 995 ‰ and Ag 999.9 ‰ are not specifically considered in the standards.

These ones, along with ISO 11426 (gold by fire assay), ISO 11427 and ISO 13756 (silver by potentiometric titration) were developed by the *ISO TC174 WG1 working group* in order to provide accurate analytical methods for the *jewellery alloys* in the range of fineness stated by the ISO 9202 standard, which ends at 999‰ and does not consider specifically the precious metals grades proper to the banking sector.

The expansion of the field of application is presently under discussion.

An example: gold in silver

Gold in silver as example of problem element

A typical example of problem element in precious metals assaying, although not necessarily the most challenging, is the one of the gold in 999‰ silver.

Several different approaches are possible and are considered here.

Precious metals analysts are used to separate gold and to accurately quantify it by fire assay and subsequent nitric acid parting, or by reduction of hydrochloric solutions by sulfur dioxide, filtering and weighing of the recovered metallic precipitate.

As we are going to see, this approach is not suitable when the gold amount involved becomes very small, yet vanishingly small.

In order to assess the suitability of the different methods it is important to get a precise idea of what we shall handle in our laboratory's beakers and volumetric flasks.

An example: gold in silver

Considering a gold concentration ranging from 1‰ down to 1 ppm the amount of the yellow metal present in a 1-gram silver sample will range from 1 milligram to 1 microgram.

Should this quantity form a single sphere of solid metal, its diameter would move from about ½ mm to ¹⁄₂₀ mm - roughly the resolution limit of the naked human eye.

Once dissolved in 100 ml volume, in order to give the matrix concentration of 10 g/l mostly used for this kind of analysis, the gold concentration would be comprised between 10 and 0.01 mg/l: still manageable for ICP-OES but requiring attention at its lower end.

gold concentration	gold weight in 1 g sample	gold sphere diameter	gold in 10 g/l silver solution
1000 ppm	1 mg	460 µm	10 mg/l
100 ppm	0.1 mg	215 µm	1 mg/l
10 ppm	0.01 mg	100 µm	0.1 mg/l
1 ppm	0.001 mg	46 µm	0.01 mg/l

An example: gold in silver

Three methods in comparison

For an assessment of different analytical approaches, samples of silver containing approximately 3, 10, 30, 100, 300 and 1000 ppm of gold were analyzed using three different methods.

For each method and each gold content, three replicates were carried out.

The weight of the sample portions was 1 g, and the final volume of the solutions analyzed by ICP was 100 ml.

As customary for accurate analyses, yttrium was used as internal standard.

Only gold was analyzed.

Gold in silver: Method 1

Method 1 (scientifically not irreproachable, but easy and effective!)

Dissolve with nitric acid, then add hydrochloric acid: silver precipitates as silver chloride while gold is dissolved by the formed aqua regia. Dilute to 100 ml, allow to settle and analyze the gold in the clear solution by ICP. 1 ml of yttrium internal standard solution is added by weight before the dissolution step.

Note:

- Basing on the achieved results it appears that segregation of gold in the silver chloride precipitate does not constitute a problem. Inversely, lead may precipitate as $PbCl_2$, making a separate analysis in nitric solution necessary.

- The use of an internal standard overcomes all problems related to the accuracy of the reference volume. The presence of silver chloride precipitate in the volumetric flask is therefore uninfluential.

Gold in Silver: Method 2

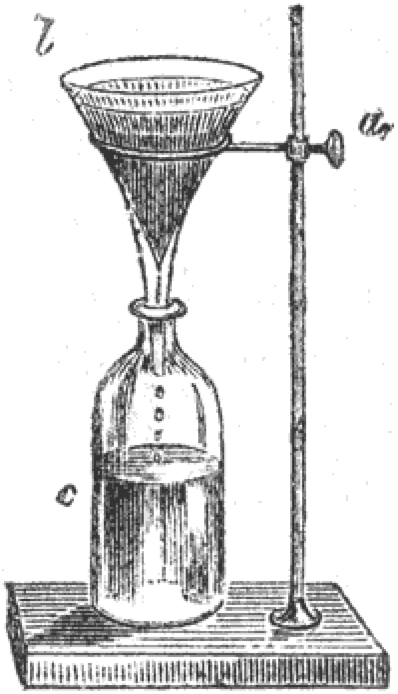
Method 2 (suggested by ISO 15096:2014)

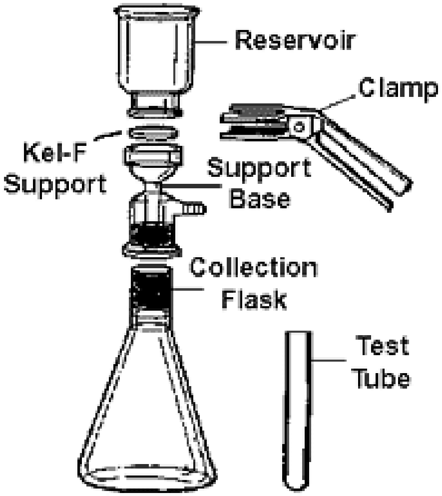
Dissolve with nitric acid, then filtrate by appropriate means, e.g. membrane filter with 0.2 um porosity. Treat the filter with aqua regia in a beaker, then transfer the gold containing solution into a volumetric flask. Analyze by ICP.
1 ml of yttrium internal standard solution is added by weight in the beakers before the aqua regia digestion.

Note:

The usual paper filters used for gravimetric analyses ("black ribbon" for coarse precipitates and "white ribbon" for finer precipitates) are not suitable here. Nitrocellulose filter membranes with pore size as low as 0.2 μm can advantageously be used; the use of Büchner or similar funnels allows a rapid filtration.

Gold in Silver: Method 2





Filter paper pore size

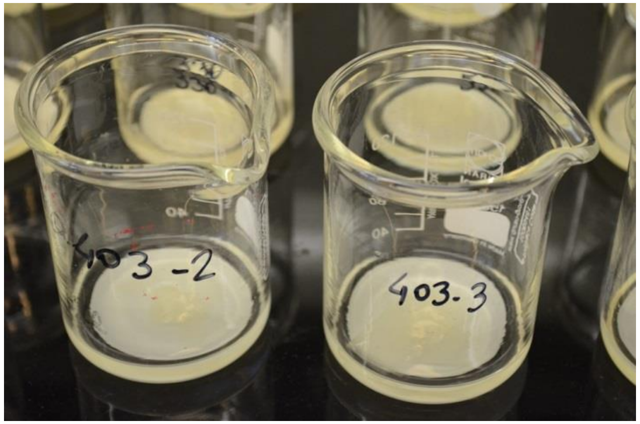
«black ribbon»	12-25 µm
«white ribbon»	4-12 µm
«blue ribbon»	2 µm

Cellulose nitrate membrane filters

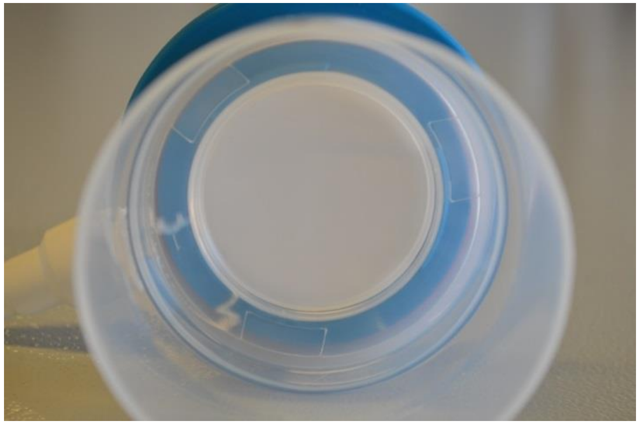
tested: 0.2 µm

Gold in Silver: Method 2

The Büchner funnel used for the tests

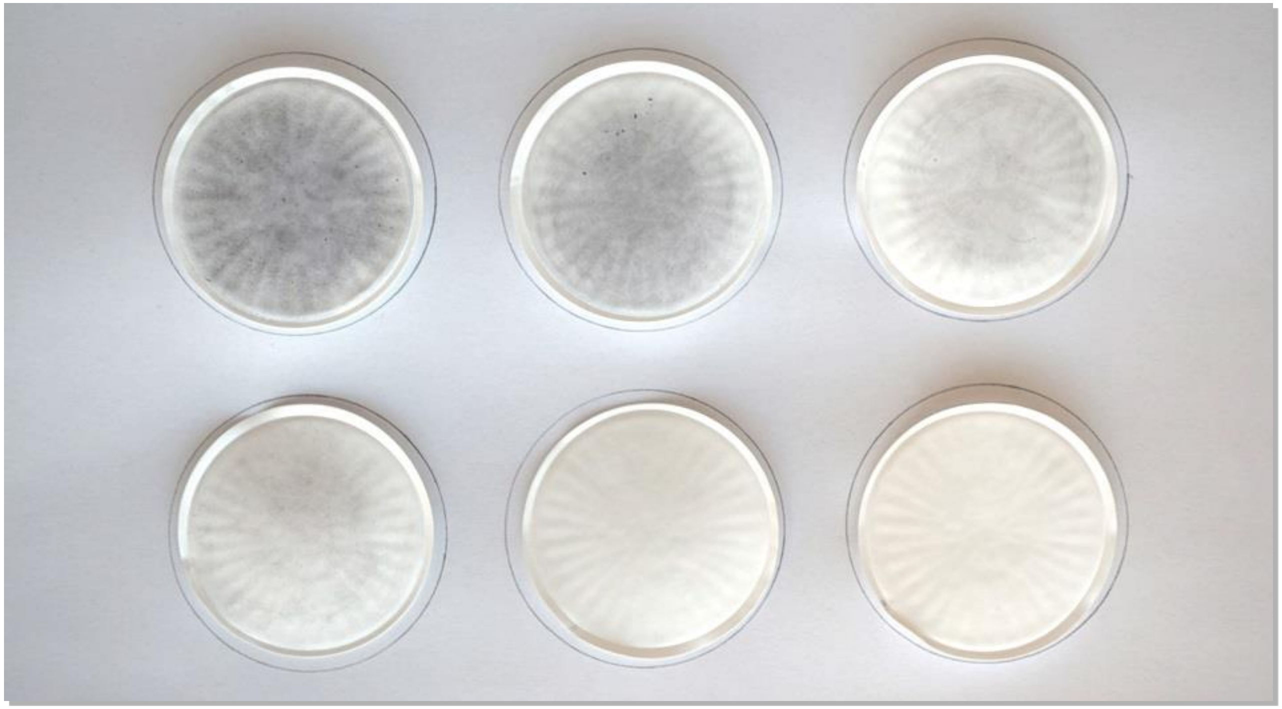


The membrane filters are treated with aqua regia



The membrane filter is held in place by a plastic lid which should prevent small particles to escape from the sides

Gold in Silver: Method 2



1 g Ag samples. From top left approx. 1000, 300, 100, 30, 10, 3 ppm Au
Cellulose nitrate membrane filters, porosity 0.2 µm, diam. 47 mm

Gold in Silver: Method 3

Method 3 (suggested by ISO 15096:2014)

Digest with nitric acid, then transfer everything into a centrifuge vessel. Centrifuge and remove the clear solution. Rinse with deionized water, centrifuge again after having rinsed with deionized water and remove again the clear solution. Repeat this procedure one time again, then add aqua regia; allow the gold to dissolve and transfer the solution into a volumetric flask. Analyze by ICP.
1 ml of yttrium internal standard solution is added by weight in the vessels prior to the aqua regia digestion.

Note:

the samples were centrifuged during 5 minutes at 3500 rpm; the clear solution was removed by using a Pasteur pipette connected to the vacuum system and always held just at the surface of the liquid in order to avoid turbulence which could lift fine particles from the bottom of the centrifuge tube.

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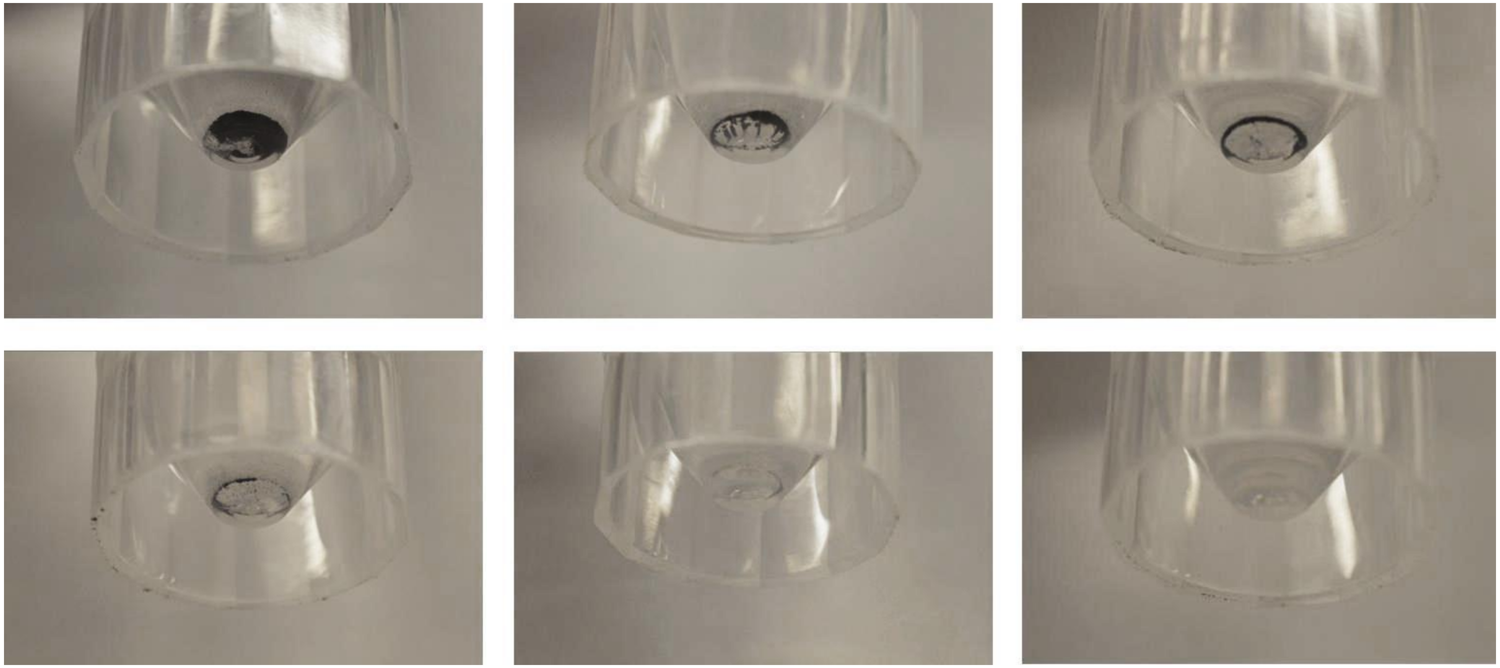
Gold in Silver: Method 3



1 g Ag samples. From top left approx. 1000, 300, 100, 30, 10, 3 ppm Au
Solutions centrifuged for 5 minutes at 3500 rpm

General assessment

	Method 1	Method 2	Method 3
practical detection limit	+	+	−−
sensitivity	+/−	+/−	−−
precision	+	+/−	−
accuracy	+	+/−	−
analyst time requirement	+	−	−−
single ICP run for all elements	−	−	−
transfer operations, loss risks	+	+/−	−−
smaller volume of gold solution	−	+	+

Note: This assessment is based on a limited number of trials without optimization of the adopted procedure and is therefore subject to possible changes.

Conclusions

- When the full ICP analysis requires separate runs with different solutions it is advisable to start from individual samples.
  This allows to optimize the process flow without needs of compromise
- Prefer procedures implying the lowest number of physical transfers of the chemical species requiring quantification.
- Use an internal standard. Add it to your samples at the earliest possible stage, in order to minimize errors related to volume measurement and to solution losses.
- Acquire specific practice and critically assess your results in order to spot potential improvements. Whenever possible participate in proficiency testing programs and in round robins.

Thanks

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