TRACEABILITY OF RESULTS OF MEASUREMENTS OF GOLD IN PRECIOUS METAL ALLOYS BY XRF

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Abstract

Traceability of the results of measurements of gold in precious metal alloys by XRF is described and the role of certified reference materials (CRMs) and reference materials (RM) explained. During the measurement process, CRMs and RMs are used twice: in the calibration of the measuring instrument (XRF spectrometer) and just before measuring each individual sample. Certified reference values used in the calibration process provide "stated references" for measurement results. Their traceability must be assured by their producer(s).
A value of a (C)RM that is measured just before each individual sample, 'only' has a correction function. It is not part of the traceability chain, but acts as a tool to reduce measurement uncertainty. In the uncertainty budget of the result, the uncertainty of the correction factor must be taken into account.
Metrological underpinning is realised when producers appropriately certify the values of CRMs. Evaluation of all processes that take place in the measured sample or (C)RM during the measurement, is not explicitly known due to the manufacturer's refusal of disclosure of the certification process of the (certified) value. This leaves doubt on the 'unbroken chain of comparisons'. The analytical community must demand this missing, but essential information from the producers.

Introduction

There are people in some countries that do not wear clothes, but there are no people who live without jewelry. Precious metals that are most commonly used for manufacturing jewelry are gold, platinum, palladium and silver. Also rhodium, iridium, ruthenium and osmium are among elements that are considered as 'precious' or 'noble metals'. Various alloys of gold and silver with copper, nickel and zinc are usually prepared in order to improve their hardness (Table 1). And what do people pay for: the 'glitter' or the real content of precious metal? In as far as the latter is an attempt towards an 'objective' evaluation of value, it requires a measurement. The reliability of the value then becomes an evaluation of the reliability of a measurement result yielding that value.

Table 1. Most often used Au alloys for jewellery

All these Au alloys shall comply with the following standards of fineness: 750, 585, 417 and 333 parts per thousand.

Au alloys		Main components of the alloy
White gold	Ni gold	Au, Cu, Ni, Ag
	Pd gold	Au, Cu, Pd
Yellow gold	"Simple"	Au, Cu, Ag
	"Magic"	Au, Cu, Ag, Zn

The process of assigning a value

Precious metal products must be assayed and marked before being placed on the market. Precious metal products must be marked with the sponsor's mark, the mark of fineness and the mark of conformity. The fineness of precious metal products is quantified by the mass fraction of precious metal in the alloy expressed in 'parts per thousand'. The old unit *carat* is still in use (24 carats represent pure gold), but not for official marking of precious metal products.

Assaying and hallmarking precious metal products is a long-standing tradition in Slovenia and since 1991, it is performed by the Metrology Institute of the Republic of Slovenia (MIRS).[1] The new Precious Metal Products Act is harmonised with the European legislation and lays down the responsibilities and the rights of all parties involved in assaying and hallmarking precious metal products in Slovenia.[2]

Precious metals can be measured by various analytical procedures most frequently using gravimetry (fire assay), titrimetry, atomic absorption spectrometry, inductively coupled plasma–optical emission spectrometry (ICP-OES) and X-ray fluorescence spectrometry (XRF).[3-5] In the Assay Laboratory of the MIRS in Celje, gravimetry and XRF are used. These methods are somehow 'complementary' since the first one is considered 'primary', but destructive, while XRF is non-destructive and quicker.

At the international level, precious metal laboratories have their Association of European Assay Officies (AEAO) with headquarters in London. This association

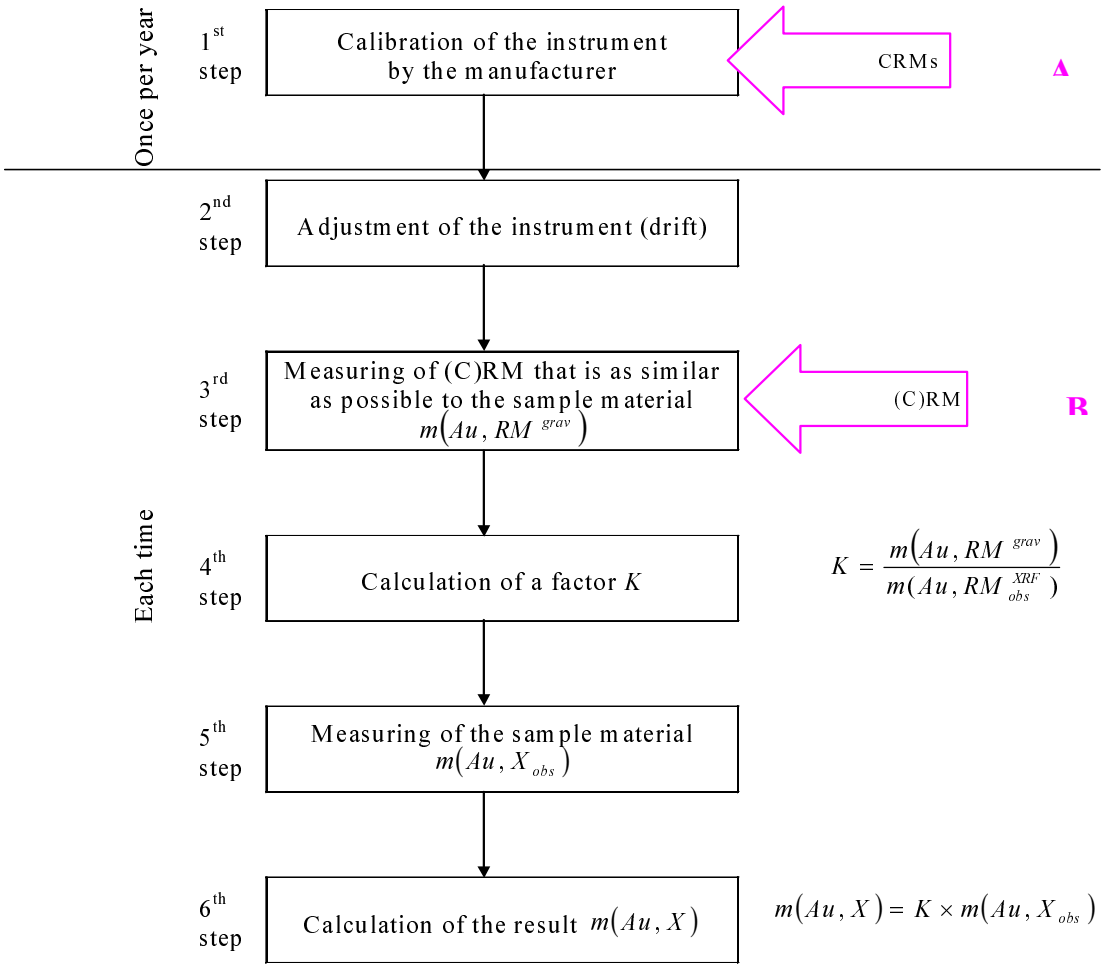
organizes proficiency testing at least once per year in co-operation with one of the national precious metal laboratories. Additionally, precious metals laboratories can also be a member of the Convention on the control and marking of precious metal products. The main objective of this Convention is to launch and operate the idea of the Common Control Mark (CCM) in the precious metals market. The only requirement to become a full member of this Convention is to be an accredited laboratory. At the moment, the Assay Laboratory of MIRS is an observer.

The analytical procedure[6]

In the analytical procedure described (Figure 1), a precious metal alloy material is bombarded with high-energy electrons from a molybdenum source. The resulting fluorescence spectrum is then submitted to identifying and measuring the measurand, calibration of the measurement procedure including measurement of a (C)RM to shrink the uncertainty of the result.[7]

First, the instrument is adjusted with a precious metal alloy that contains silver and copper. Two peaks are observed. The peak found at lower energy is connected to the Cu peak, with the energy of 8.48 keV, while the peak detected at higher energy values is connected to the presence of Ag peak at 22.16 keV. By this procedure the energy scale is defined, expressed in keV. After that, the (C)RM with a matrix as similar as possible to the sample material, is measured and calculation of a correction factor K with its uncertainty is performed. The correction factor is the quotient of the (certified) mass fraction $m(Au, RM^{grav})$ of gold in the RM measured gravimetrically and the observed mass fraction $m(Au, RM_{obs}^{XRF})$ of gold in the RM measured by XRF.

Figure 1. Procedure for measuring the mass fraction of Au in precious metal alloys by XRF



$m(Au, RM^{grav})$	Mass fraction of Au measured (preferably) by gravimetry in (C)RM that is as similar as possible to the sample material
$m(Au, RM_{obs}^{XRF})$	Mass fraction of Au in the same (C)RM as above measured by XRF
$m(Au, X_{obs})$	Mass fraction of Au in the sample material measured by XRF (before correction)
$m(Au,X)$	Result of mass fraction of Au in the sample material

$$K = \frac{m(Au, RM^{grav})}{m(Au, RM_{obs}^{XRF})}$$

Then, the unknown mass fraction $m(Au, X_{obs})$ of gold is measured in the sample of material X and corrected by using the correction factor *K* thus leading to the final result for $m(Au, X)$:

$$m(Au, X) = K \times m(Au, X_{obs})$$

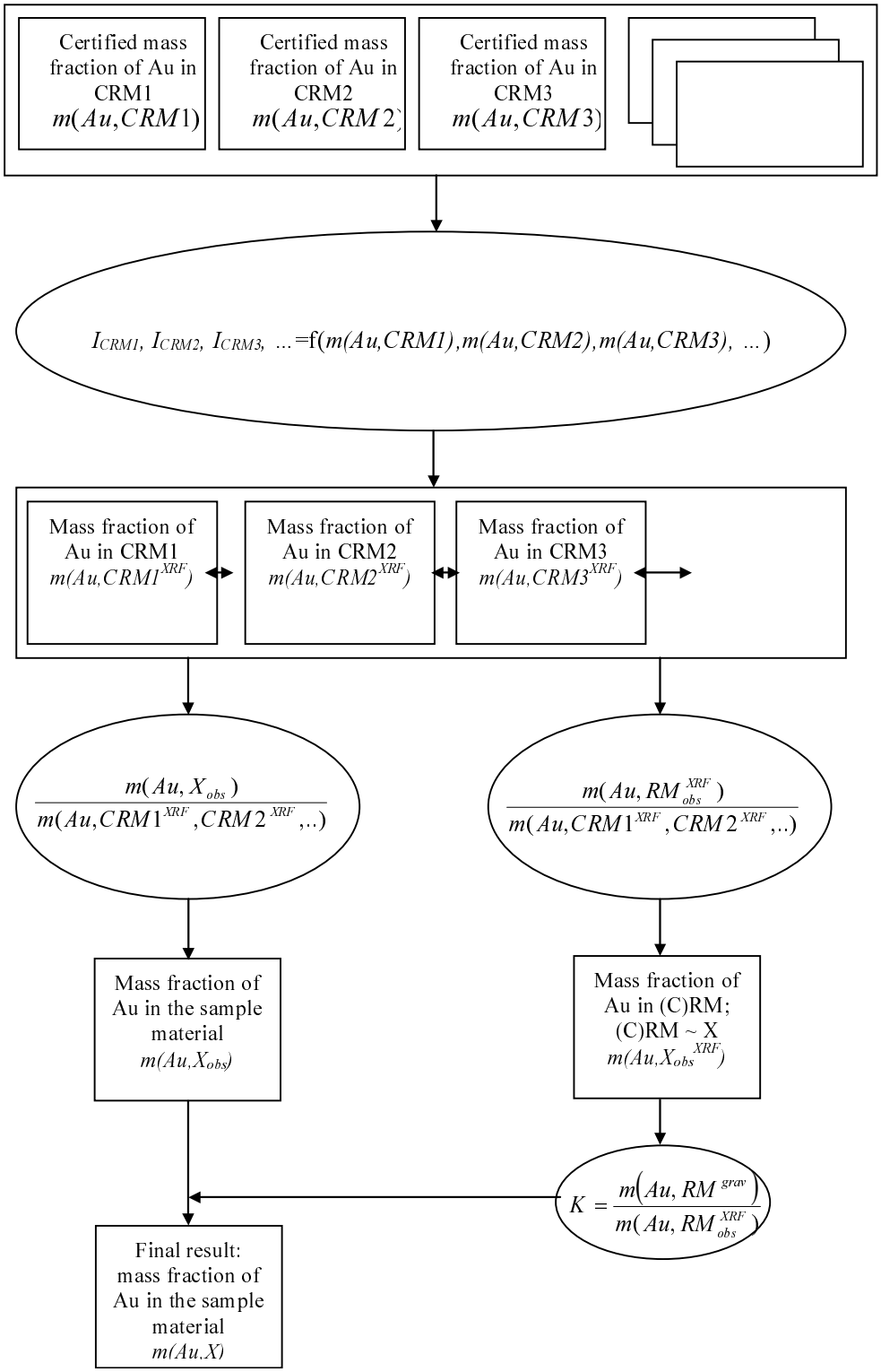
In search of the traceability of the results

(C)RMs are used twice in the analytical procedure (Figure 1). First, *when calibrating the measurement procedure* and second, *just before the measurement of the sample*. In Figure 1 these two stages are clearly indicated as A and B.

It does not happen very often that (C)RMs of various composition and quality appear in the same analytical procedure twice. And when they do, that is usually in the calibration procedure or in the validation process. Obviously, the situation in the analytical procedure under examination here is different and, at first sight, it looks as if traceability of the results is assured twice. After the present examination of the basic principles, the way out proves to be very clear and surprisingly simple.[8-17]

Leaving aside the traceability chain of the CRM, the values of which are the responsibility of their producers, the traceability chain of the measurement result obtained on the sample, is realized by the calibration of the measurement procedure (here practically reduced to the calibration of the instrument) that is regularly performed by the manufacturer using values from several CRMs. In doing so, an electrical current is actually measured, and converted to the mass fraction of gold in the matrix of each CRM. The exact mathematical equation converting the actually measured quantity (i.e. the electrical current) into the claimed quantity (i.e. the mass fraction of gold) is not known because of intellectual property reasons. Calibration of the instrument is obviously the only point in time in this measurement process where traceability of the results is established. The role of the (C)RM at point B is different, and that becomes evident if we consider the two sequential actions as two different measurement processes (Figure 2).

Figure 2. Establishment of the traceability of the results (mass fraction of gold in precious metal alloys) in an analytical procedure using XRF



Evaluation of the uncertainty of the result

(C)RM (to determine a correction factor) and sample are measured sequentially (Figure 2). Obviously, that is 'only' a *correction* necessary because of calibration of the instrument is done by means of CRMs which have matrices (sometimes quite) different from those of the sample material. Therefore, the role of the CRM value at this stage is not establishing traceability, but rather minimising measurement uncertainty. The uncertainty of the correction factor $U(K)$should also be taken into account in the evaluation of the combined uncertainty of the end result. It would be interesting to compare uncertainties of the results $U[m(Au,X)]$ when using, and when not using, the correction factor, and explain these values to the end users of the results.

$$\frac{U[m(Au,X)]}{m(Au,X)} = \frac{U(K)}{K} + \frac{U[m(Au,X_{obs})]}{m(Au,X_{obs})}$$

Conclusion

In the analytical procedure investigated, the traceability chain of the result is apparently based on the instrument's manufacturer work only. However, it is the responsibility of the analysts to request all information needed in order to establish the traceability of his/her measurement results. He/she is therefore entitled to receive all information (from the manufacturer) to do so. As seen above this is not done in practice: some 'undisclosed' modeling is performed. The exact modeling function is not known to the analyst and the whole mechanism of converting actually measured electrical currents into the claimed quantity is very poorly described by the manufacturer. It is obvious that manufacturers must provide all the information relevant for the clear establishment of traceability of the results measured by XRF.

References

a According to the trend of the revision of VIM, 'measurement procedure' will be used instead of 'analytical procedure' in the future.

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Povzetek

V prispevku je opisana sledljivost meritev masnega deleža zlata v zlitinah plemenitih kovin z metodo XRF in opredeljena vloga certificiranih referenčnih materialov (CRM) in referenčnih materialov (RM). CRMi in RM se v analitskem postopku uporabijo dvakrat: v postopku kalibracije merilnega inštrumenta (XRF spektrometer) in tik pred meritvijo vsakega posameznega vzorca. Certificirane referenčne vrednosti upoštevane v okviru kalibracijskega postopka zagotavljajo ustrezno merilno sledljivost, pri čemer mora proizvajalec CRM zagotoviti ustrezno sledljivost meritev, opravljenih v certifikacijskem postopku. Vrednost izmerjena za (C)RM tik pred vsakim posameznim vzorcem, pa služi 'zgolj' za izračun ustreznega korekcijskega faktorja. Ta meritev torej ne vzpostavlja sledljivosti, temveč služi kot 'orodje' za zmanjšanje merilne negotovosti rezultata, pri čemer moramo upoštevati tudi negotovost korekcijskega faktorja.

Ustrezna metrološka podpora je zagotovljena, če proizvajalec CRM ustrezno zagotavlja sledljivost njegove vrednosti. V opisanem primeru (zaradi pomanjkljivih podatkov izvajalca o zagotavljanju sledljivosti CRMi) ostaja dvom v "neprekinjeno verigo primerjav" – sledljivost rezultatov. Zatorej je (tudi) dolžnost analitikov, da vztrajajo pri zahtevah o neobhodno potrebnih informacijah o sledljivosti vrednosti CRM.