Gold assay with Knudsen effusion mass spectrometry

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A B S T R A C T

Commercial 18 carat (ct) gold alloys along with pure coinage metals have been studied with Knudsen effusion mass spectrometry. Isotopic fractionation in vapour phase and the enthalpies of vaporization were estimated for Au, Ag and Cu samples. The assaying of the gold content was carried out by means of calibration with respect to standard reference alloys measured with energy dispersive X-ray spectroscopy. The accuracy of the gold determination resulted of about 1.5 wt.‰ in the ternary Au–Ag–Cu alloy.

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1. Introduction

Nowadays, more than 75% of the global gold output is processed in the jewellery industry, which means that for international economics accurate determination (assay) of the gold content (fineness) is very significant. An ideal method of assaying should be accurate at the level of one part per mil (1‰), fast and reasonably priced. Other important factors are the size of the samples, consistency and reliability of the measurements, determination of all components, whether the method is destructive or non-destructive, etc.

The traditional cupellation (fire assay) [1] is the method used worldwide for gold determination. It is a very ancient technique mentioned even in the Bible. In its present form, cupellation remains the most accurate method available and serves as the standard technique against which all others are compared. It is covered by the ISO standard ISO 11426:1993.

In recent years, the need for fast and accurate gold assaying methods stimulated the testing of a number of modern analytical techniques such as energy dispersive X-ray fluorescence (XRF) [2,3], glow discharge and inductively coupled plasma-optical emission and mass spectrometric methods [4,5], laser-induced breakdown spectroscopy [6,7], etc. For details about these and other instrumental techniques, applying to determination of precious metals, the reader is addressed to the monograph of Van Loon and Barefoot [8].

Energy dispersive X-ray fluorescence spectroscopy has gained most popularity now, finding service in both jewellery factories and in assay laboratories. There are many producers of XRF instruments on the market. According to Ref. [9], XRF can measure the title (gold content) of an alloy with an accuracy of 0.75 wt.‰ under optimum conditions, however typical accuracy is about 2–5‰. This technique is non-destructive, determines all elements excepting very light ones (C, B, Be), but only in the near-surface layer, about 5–10 μm in depth. Electroplating or chemical treatments, modifying the surface composition, distort the results of XRF. For optimum measurements, the sample surface should be clean, flat and polished, and at least 3 mm in diameter. Curved surfaces reduce accuracy since the emitted X-rays are randomly scattered off.

Therefore, the development of novel methods for gold assaying is still ongoing. Recently, SIMS and mass-resolved ion scattering spectrometry have been applied to the characterization of electrodeposited Au, Pd and Ru coatings [10], and medieval Venetian gold coins [11]. These techniques are very sensitive and offer an advantage of sputter depth profiling within a few micrometers in depth, however, they are scarcely suited for the determination of the bulk elemental content.

Knudsen (cell) effusion mass spectrometry (KEMS) [12,13] has proved to be a powerful tool for determination of thermodynamic properties of different materials, including gold, silver and copper

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[14]. As far as we know, there are no publications in the literature about gold assay with KEMS. In this paper, we report a detailed study of vaporization of the basic coinage metals (Au, Ag, Cu), and the results of the KEMS quantification of ternary and quaternary gold alloys containing also zinc and tin.

2. Experimental

We investigated commercial gold alloys of 18 carats (750 wt.‰ gold content) along with pure (999 wt.‰) gold, silver and copper samples. Hereafter, these metals, characterizing by a fully filled electron d-zone, are collectively referred as "coinage" since the grouping of precious or noble metals does not include copper (silver is also not considered as a precious metal by some authors [1,8]). Generally, gold title is expressed in weight parts per mil (wt.‰) or in the standard units called carats (not to be confused with the weight carat equal to 200 mg and used for a variety of materials, including diamonds and pearls). Pure gold corresponds to 24 carat (ct) according to the Common Control Mark scale. Along with basic coinage metals some additional (dopant) metals like zinc, tin, nickel, etc. can be found in jewellery alloys. These additives influence the mechanical properties and coloration of alloys. Some physical and thermal properties of coinage and dopant metals are listed in Table 1.

The measurements reported in the present work were carried out with a custom-built Knudsen effusion mass spectrometer. The schematic configuration of the instrument is shown in Fig. 1.

A linear time-of-flight analyser LFT 10 with mass resolution $M/\Delta M \geq 500$ (FWHM) was developed by Stefan Kaesdorf [15]. Electron impact ionization ion source ($E_{el} = 5$–90 eV) is equipped with two permanent magnets ($B = 10^{-2}$ T) which guide the electron beam through the ionization zone. A two-stage extraction scheme according to Wiley–McLaren [16] compensates for the difference in the starting position of the ions. The field-free drift part has a length of 588.5 mm. For the efficient detection of heavy molecules with masses up to 1000 m/z the ions are accelerated to a maximum energy of 8 keV before hitting the detector (a two-stage microchannel plate by Burle [17] with 25 mm in active diameter). The software TOF 5.0 allows data acquisition, evaluation and treatment.

A high-temperature effusion cell HTC-40-2-220-SHM-WK with control unit CU-2404-S1-AC was developed by CreaTec Fisher [18]. The control unit contains a precise PID controller in combination with an AC power supply (max output power of 700 W). A 2 cm³ cylindrical crucible is heated up to 2000 °C by a self supported tungsten wire. We used crucibles made in graphite (PRG). The cell temperature was measured using a calibrated W–Re (5–26%) thermocouple. The temperature stability was found to be ca. ±0.5 °C.

Metal vapours, effusing through a small cylindrical orifice of 1 mm in diameter, are collimated with a 2 mm aperture placed in the space between effusion cell and ionization chamber of the ion source. The manual shutter allows interrupting the molecular beam. The Clausing factor, k, of the effusion orifice, estimating in accordance with [19,20] as

$$k = \left[0.98441 + 0.00466\left(\frac{l}{r}\right)\right] \times \left[1 + 0.46034\left(\frac{l}{r}\right)\right]^{-1}, \qquad (1)$$

where l is height and r is radius of the orifice, amounts to 0.90 in our experiments, and the sample-to-orifice squares ratio is found to be $s = 25$–35.

The system includes two vacuum chambers, one for sample vaporization and the other for mass spectra measurements. The chambers are separated from each other by a UHV gate valve and evacuated using turbo-pump assemblies by Adixen [21]. The sample chamber has an extra by-pass pumping line for fast sample loading. During experiments the pressure in the analytical chamber was maintained at the level of $(0.5$–$1) \times 10^{-7}$ mbar. Full range cold cathode gauges were used for the pressure measurements in the chambers.

No special sample preparation is required in our experiments beyond simple cleaning by rinsing in ethanol. The sample weights 50–250 mg; about 50–60% of their initial weights were found to remain into the cell after the ending of the measurements. The measurements were carried out over the 500–2000 °C temperature range depending on the sample composition. The cell was maintained at a constant temperature while four mass spectra in a range of 1–400 m/z were recorded sequentially. The last spectrum was recorded with closed shutter (denoted as blank spectrum). The resulting data are calculated as a difference between mean values estimated from the 1st to 3rd spectra and the blank spectrum. Electrons of 20 eV were used in the ion source to ionize the vapours effusing from the cell.

3. Results and discussion

3.1. Evaporation of the pure coinage metals

Mass spectra of the positive ions measured under vaporization of pure Cu, Ag and Au are shown in Fig. 2. The weight of all samples is ca. 100 mg. Mass resolution, $M/\Delta M$ (FWHM), is 605, 790 and 850 for ^{63}Cu, ^{107}Ag and ^{197}Au, respectively. Blank spectra for the silver and gold exhibit no peaks in the range of interest (not shown in Fig. 2b and c). For the copper sample, a peak of residual gases at m/z of 64, between the isotope peaks ^{63}Cu and ^{65}Cu, is detected (shown in Fig. 2a with a dot line). For the silver sample at the temperature higher than 1400 °C along with the atomic ions the molecular ion species Ag$_2^+$ were detected but in a little quantity, with peak intensity ratio ^{107}Ag/(^{107}Ag^{109}Ag) ≥ 500 at 1500 °C.

Fig. 3 shows the peak intensities of the main isotopes of Cu, Ag and Au against the relative temperature of the effusion cell. The term "peak intensity" means here the peak area calculated above the threshold of 5 counts. The relative temperature is calculated as $T_{rel} = T/T_1$, where T is the actual temperature of the effusion cell and T_1 refers to the temperature necessary to reach the 1 mbar vapour pressure of the elements [22] (see Table 1). Both temperatures are in the centigrade scale (°C). The introduction of the relative temperature facilitates the presentation of our experimental results in the graphical form.

For the copper and silver samples we measured the isotopic fractionation in the vapour phase versus the relative temperature of the effusion cell. Commonly, the isotopic fraction δ specifies the rela-

Table 1
Physical and thermal properties of coinage and dopant metals formed commercial gold alloys

	Au	Ag	Cu	Zn	Sn
Atomic number	79	47	29	30	50
Molecular weight (g mol⁻¹)	196.97	107.87	63.55	65.39	118.71
Ionization energy (eV)	9.23	7.58	7.73	9.39	7.33
Melting point (°C) [22]	1063	961	1084	420	232
Temperature (°C) necessary to reach 1.33 mbar vapour pressure [22]	1707	1337	1628	492	1609
Main isotope and its abundance ratio (%) [29]	^{197}Au/100	^{107}Ag/51.84	^{63}Cu/69.17	^{64}Zn/48.6	^{120}Sn/32.59