



Gold assay with Knudsen effusion mass spectrometry

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ABSTRACT

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 (finesness) 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 ($E_{ei} = 5\text{--}90$ 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

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

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 $s = 25\text{--}35$.

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 $(0.5\text{--}1) \times 10^{-7}$ 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 ⁶³Cu, ¹⁰⁷Ag and ¹⁹⁷Au, 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 ⁶³Cu and ⁶⁵Cu, 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 $^{107}\text{Ag}/(^{107}\text{Ag}^{109}\text{Ag}) \geq 500$ 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

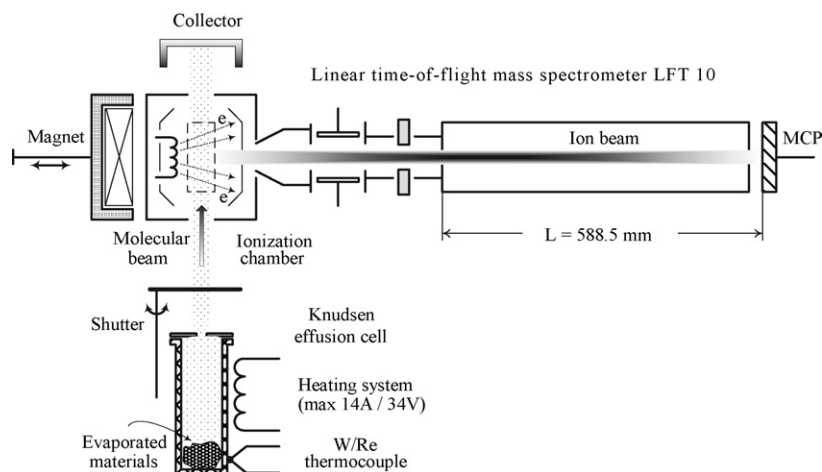


Fig. 1. General arrangement of the instrument, not to scale.

tive deviation of the measured abundance ratio of two isotopes of an element from the corresponding standard value of this ratio. The magnitude of δ is expressed per mil via

$$\delta = \left(\frac{R_{\text{exp}}}{R_{\text{st}}} - 1 \right) \times 1000, \quad (2)$$

where R_{exp} and R_{st} denote the experimental and standard ratios of the heavy-to-light isotope abundances ($^{65}\text{Cu}/^{63}\text{Cu}$ and $^{109}\text{Ag}/^{107}\text{Ag}$ in our case). Hence, a negative value of the δ -parameter signifies a depletion of the heavy isotope relative to the standard.

As indicated in Fig. 4, within the limits of the experimental error ($\pm 10\%$), the magnitude of the isotopic fractionation $\delta^{109}\text{Ag}$ tends to zero over all the temperature range, while the $\delta^{65}\text{Cu}$ value increases with an increasing temperature. This phenomenon could be interpreted as due to artefacts associated with the peak intensities rather than the peak masses. Heavy isotopes both of silver and, especially, of copper are less intense than the light ones (a standard abundance $R(\text{Ag})_{\text{st}} = 0.929$ and $R(\text{Cu})_{\text{st}} = 0.4457$). Due to the probable saturation of the detector in our experiments, it may be that with increasing temperature, and increasing total peaks intensity as well, the light copper isotope could be suppressed in a greater extent than the heavier one.

In general, the vapour pressure of isotopes depends on their masses on $-(1/2)$ degree (see, e.g., Ref. [23]). For this reason, the heavier isotope could be depleted in vapour flux relative to the standard isotopic abundance. Quantum-mechanical calculations by Teller et al. [24] confirmed this conclusion, however, in the same publication the situation when under evaporation of the C_6D_6 and C_6H_6 mixture the vapour was enriched with the compound on base of deuterium is also discussed.

Detailed discussion of the possible sources for the isotopic fractionation in the vapour phase is beyond the scope of the present paper. At this stage, we consider isotopic fractionation measurements as a means of testing of our instrument. Therefore, we used the data shown in Fig. 4 for the temperature optimization of the effusion cell, assuming that under the minimum magnitude of the

δ -parameter, the accuracy of the gold assay should be maximal. The optimal temperatures in our experiments are approximately coincided with T_1 , i.e., with the temperatures corresponding to the 1 mbar vapour pressure of the pure components.

The best test for proper operation of a Knudsen cell instrument is determination of the enthalpy of vaporization. The Van't Hoff equation in chemical thermodynamics [25] relates the changes in temperature to the change in the equilibrium constant given the enthalpy. It assumes that the enthalpy change is constant over the temperature range as

$$\ln(K) = -\frac{\Delta H^\circ}{R} \left[\frac{1}{T} \right] + \frac{\Delta S^\circ}{R}, \quad (3)$$

where K is the equilibrium constant at absolute temperature T , ΔH° and ΔS° are the enthalpy and entropy changes, respectively, and R is the gas constant ($R = 8.31447 \text{ J/mol K}$).

For a simple vaporization reaction like $\text{A(s)} = \text{A(g)}$ the equilibrium constant $K = p(\text{A})$, where p is the pressure of A-element in a Knudsen cell. Since $p(\text{A}) \propto I(\text{A}) \cdot T$ (for details, see, e.g., Ref. [14]), where I is the ion intensity of A-element, the enthalpy of vaporization may be determined from the slope of $\ln(I \cdot T)$ plotted against the reciprocal absolute temperature without knowledge of any other parameters. Conversely, these extra parameters must be known in order to determine ΔS° .

The Van't Hoff plots for the main isotopes of pure coinage metals are shown in Fig. 5. The results of the ΔH° estimation at the average temperature of the measurements are presented in Table 2. We also show there the values of ΔH° calculated at the same temperatures using Ref. [26] and the currently accepted values of the enthalpy of vaporization of pure Cu, Ag and Au at room temperature [27]. Some discrepancy between our results and the literature values can be interpreted as due to the fact that the sample vaporization in our instruments is not perfectly in equilibrium from a thermodynamic point of view. It is likely that an error is introduced as the effect of the modest value of the sample-to-orifice squares ratio, which is $s = 25\text{--}35$ (should be 10^2 , at least, according to Ref. [12]). Some

Table 2
Enthalpy of vaporization of pure coinage metals

Sample	Enthalpy of vaporization ΔH° (kJ mol ⁻¹)		
	Our experimental data	Calculated data [26]	Currently accepted values at 298 K [27]
Copper	365 ± 20 (1923 K)	309.8 (1900 K)	367.0 ± 0.9
Silver	260 ± 7.5 (1623 K)	261.2 (1600 K)	284.5 ± 1.3
Gold	395 ± 15 (1823 K)	343.4 (1800 K)	337.6 ± 1.2

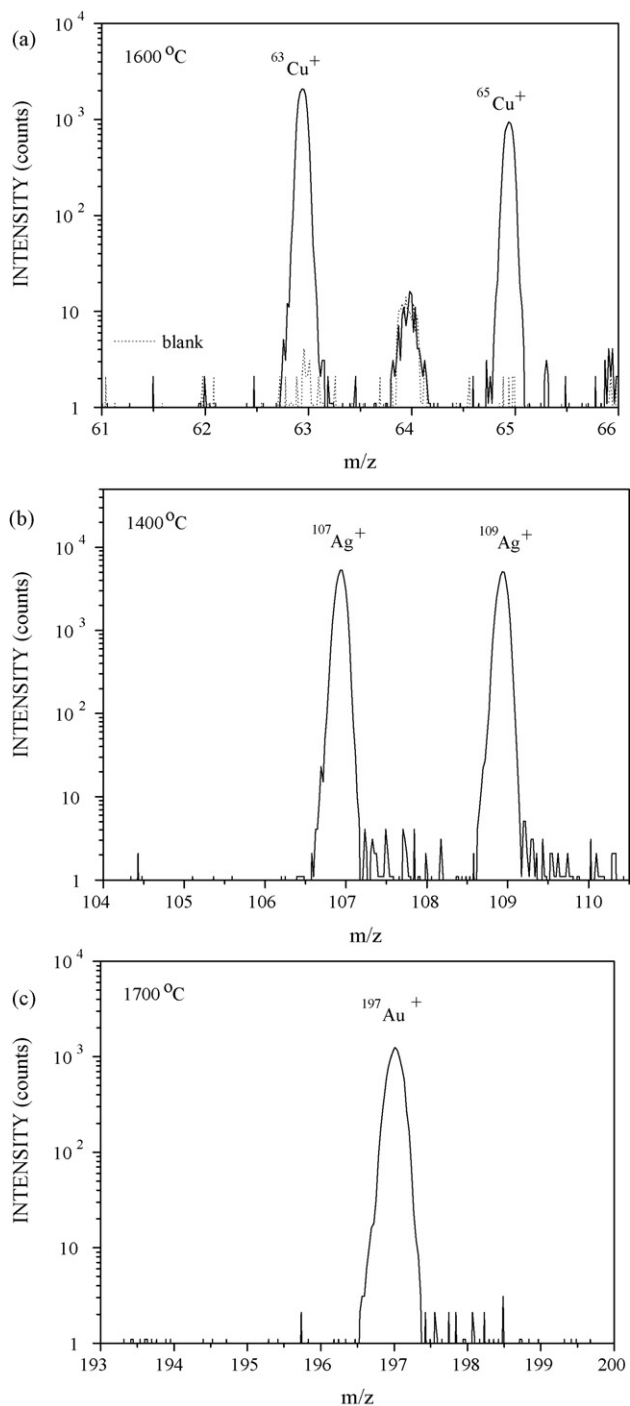


Fig. 2. Mass spectra of the positive ions measured under vaporization of pure copper (a), silver (b) and gold (c). For the Cu sample the blank spectrum registering with the closed shutter is shown too. The temperature of the effusion cell is indicated at the upper left corner of every panel.

other sources of error could be (i) the imperfect vapour-tightness of our cell that allows uncontrolled loss of analysed materials during evaporation, and (ii) a rather high pressure into the cell, well above 10 Pa, that is an upper limit of molecular flow through the cell orifice under the Knudsen effusion conditions.

3.2. Evaporation of the jewellery alloy

We studied three different commercial 18 ct gold alloys, in two samples of every alloy. The sample denoted in our experiments

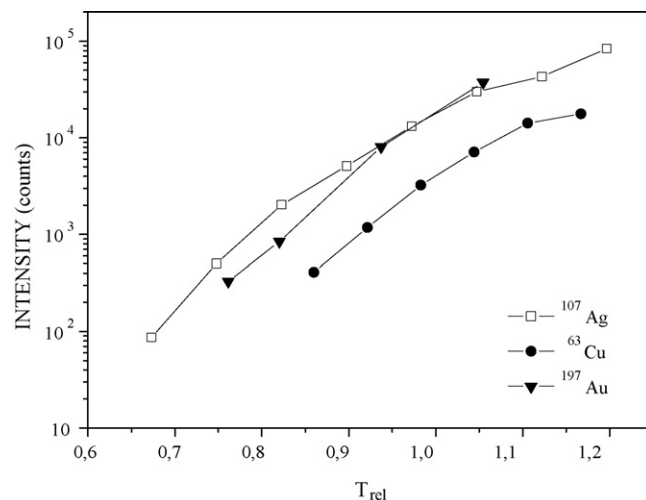


Fig. 3. Peak intensities of the main isotopes of coinage metals versus the relative temperature. The temperature of the effusion cell is ranged within 900–1900 °C.

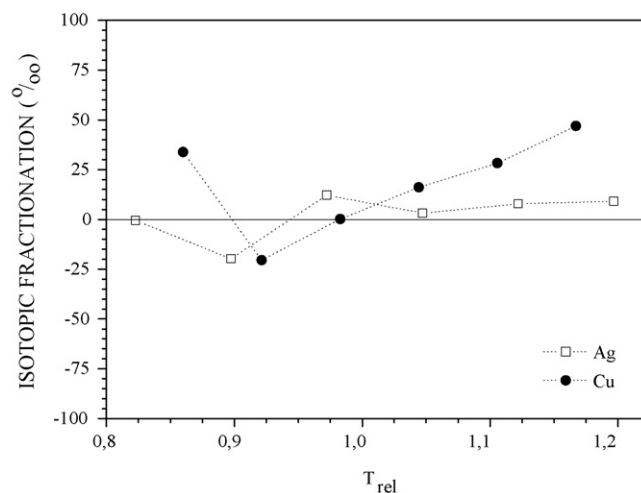


Fig. 4. Isotopic fractionation $\delta^{65}\text{Cu}$ and $\delta^{109}\text{Ag}$ measured at the different relative temperatures. The temperature of the effusion cell is within the range of 1400–1900 °C for copper and of 1100–1600 °C for silver.

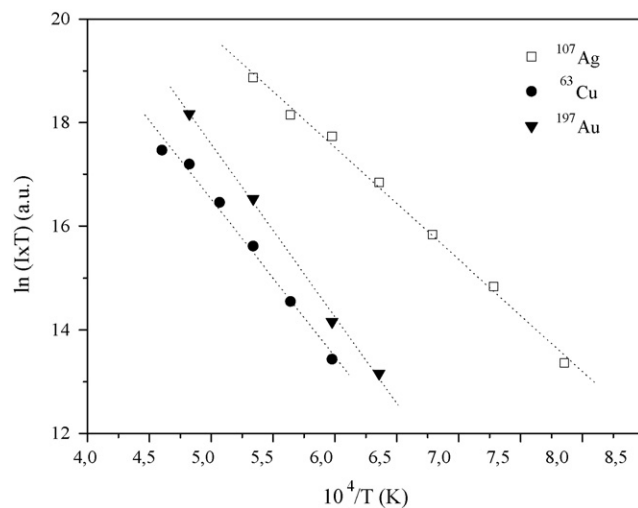


Fig. 5. The Van't Hoff plots for the main isotopes of pure coinage metals. The temperature of the effusion cell is within the range 1400–1900, 1100–1600 and 1300–1800 °C for copper, silver and gold, respectively.

as Alloy 1 is a ternary Au–Ag–Cu alloy; Alloy 2 and Alloy 3 are four-component alloys with Zn and Sn additives, respectively. The relative weight content W (wt.%) of the components was examined by energy dispersive X-ray spectroscopy (EDS) [8] at the assay office in Arezzo (Italy). The accuracy of gold determination was ca. 1%, while for the other components it was within 1–5%.

The dependencies of the ion peak intensities of the main isotopes of Au, Ag, Cu, Zn and Sn against the relative temperature of the effusion cell are shown in Fig. 6. Mass spectra of the positively charged ions of Zn and Sn measured for the four-component gold alloys are presented in Fig. 7. Mass resolution $M/\Delta M$ (FWHM) is 820 for ^{64}Zn (Alloy 2) and 950 for ^{120}Sn (Alloy 3). We should point here that $M/\Delta M$ values estimated in our experiments for the vapour flux (see also Fig. 2) are better than the nominal value $M/\Delta M = 500$ determined for a LFT 10 analyser in the residual gas analysis mode. It means that the molecular beam, emerging from the effusion cell, is better localized into the space of the ionization chamber than randomly moving gas molecules, and the space focusing regime according to Wiley–McLaren scheme perfectly suits for measurements of evaporated species.

The blank spectrum of zinc (a dot line in Fig. 7a) exhibits intense features also with the closed shutter. The zinc content in the alloys is low, slightly less than 20 wt.%, and its ionization potential is high (9.39 V). Thus, we expect to measure zinc at higher relative temperature of the effusion cell ($T_{\text{rel}} \geq 1.5$) in comparison to other components. Since our cell is not totally vapour-proof, the evaporated species effuse not only through the outlet orifice and could get to the analytical chamber around the closed shutter, especially, when the partial pressure of the component into effusion cell is very high (for Zn at 700–800 °C it reaches hundreds mbar).

3.3. Quantification on the gold alloys

The determination of the sample content is carried out by calibration with respect to standards quantified with other methods. One of the samples of every alloy is considered as a “reference sample” (Table 3), and for each component of this sample the KEMS elemental sensitivity factors were evaluated using the data presented in Fig. 5. Then, we applied these factors for quantification of another, “determined sample” belonging to the same alloy grouping and compared the results of our calculation with the data obtained by EDS (Table 4). The weight of the reference and determined samples is different in our experiments since we would like to see how this parameter influences on the accuracy of assaying.

At first, we used pure metals as standards. However, this approach yielded low precision of quantification, and vaporization of pure zinc resulted in heavy contamination the ion source and the analytical chamber.

The elemental sensitivity factor of the i -component is determined as

$$\text{SF}_i = \left(\frac{I}{N} \right)_i, \quad \text{counts (at. \%)}^{-1} \quad (4)$$

where I is the peak intensity of the main isotope ions and N is the atomic concentration (per mil).

Table 3

Reference 18 ct gold samples: W is a relative weight content of the components, wt.%; SF is a sensitivity factor, counts per at.%

Alloy	Weight (mg)	Au		Ag		Cu		Zn		Sn	
		W	SF	W	SF	W	SF	W	SF	W	SF
Alloy 1R	210	769.0	5.11	122	192.6	109	41.05	–	–	–	–
Alloy 2R	100	754.5	12.18	110.5	74.52	116	20.74	19	224.4	–	–
Alloy 3R	165	749.5	26.60	149	332.4	67	47.59	–	–	34.5	41.2

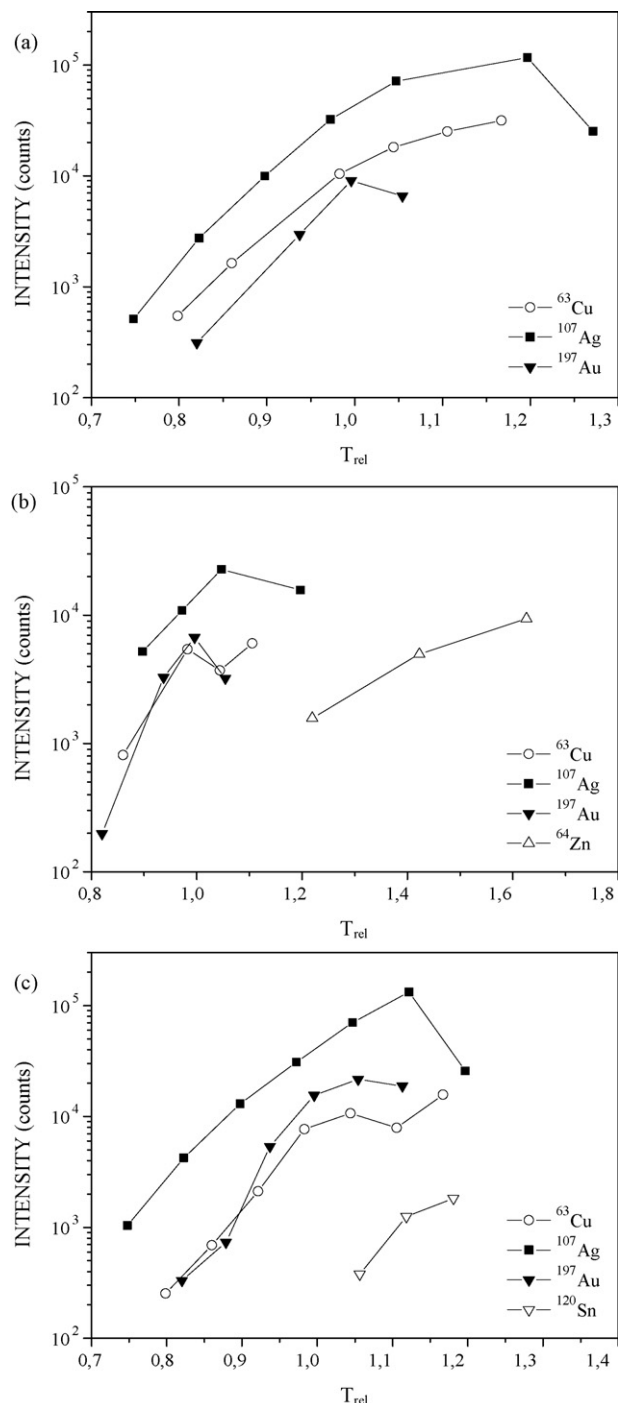


Fig. 6. Peak intensity of the main isotopes of Cu, Ag, Au, Zn and Sn against the relative temperature measured under vaporization of the commercial 18 ct gold Alloy 1R (a), Alloy 2R (b) and Alloy 3R (c). The temperature of the effusion cell is in the 600–1900 °C range.

Table 4

Determined 18 ct gold samples: W is a relative weight content of the components, wt.%; EDS is the concentration measured by EDS; KEMS is the results obtained with Knudsen effusion mass spectrometry

Alloy	Weight (mg)	W_{Au}		W_{Ag}		W_{Cu}		W_{Zn}		W_{Sn}	
		EDS	KEMS	EDS	KEMS	EDS	KEMS	EDS	KEMS	EDS	KEMS
Alloy 1D	145	760.5	759	123	137	116.5	104	–	–	–	–
Alloy 2D	230	779.0	766	116	107	85	110	20	17	–	–
Alloy 3D	155	737.0	744	163	155	67	66	–	–	33	35

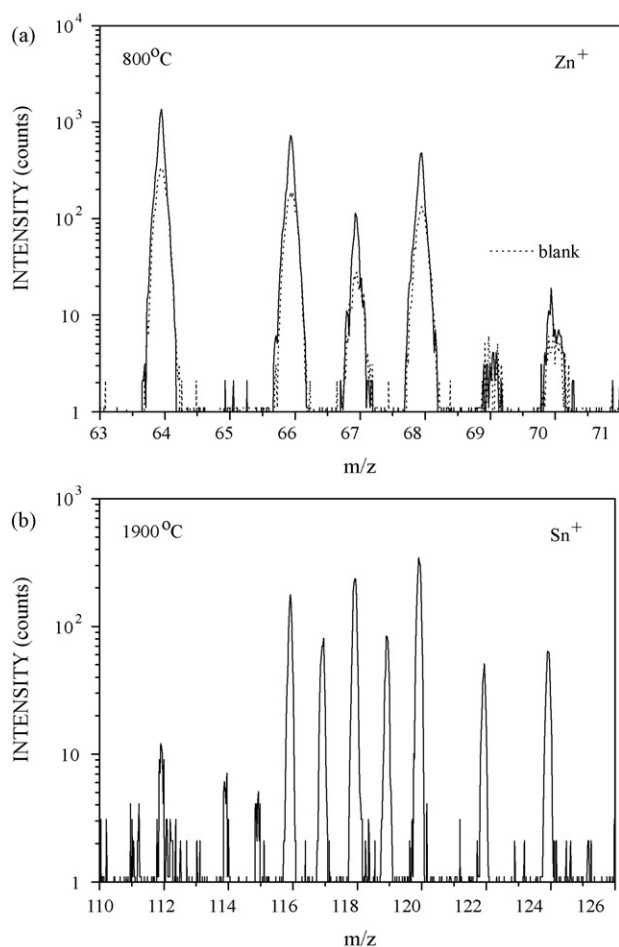


Fig. 7. Mass spectra of the positive ions of zinc (a) and tin (b) measured under vaporization of the quaternary Alloy 2R and Alloy 3R, respectively. For the zinc-contained sample the blank spectrum registered with the closed shutter is shown too. The temperature of the effusion cell is indicated at the upper left corner of every panel.

Atomic concentration and weigh content W is related by

$$N_i = \frac{W_i/M_i}{\sum_{i=1}^n (W/M)_i} \times 1000, \quad \text{at. \%} \quad (5)$$

where M is the molecular weight (see Table 1) and n is the number of the components.

The recalculation of atomic concentration to weight content is performed via

$$W_i = \frac{(N \cdot M)_i}{\sum_{i=1}^n (N \cdot M)_i} \times 1000, \quad \text{wt. \%} \quad (6)$$

The relative error in the determination of elemental sensitivity factors SF_i (Table 3) does not exceed $\pm 1\%$ for gold and silver, $\pm 1.5\%$ for copper and $\pm 2.5\%$ for zinc and tin. The optimal temperature of the effusion cell, at which SF -values is determined, was found to

be 800°C for zinc, 1400°C for silver, 1600°C for copper, 1700°C for gold and, finally, 1900°C for tin.

The accuracy in gold assay in our experiments involving Knudsen effusion mass spectrometry with the EDS calibrated standards was found to be better than 2 wt.% for the ternary alloy and of about 13 wt.% for the quaternary alloys. For Ag and Cu we estimate the accuracy of determination within 25 wt.%, and for Zn and Sn it is 3 wt.%. Since EDS also needs adequate calibration and a sampling depth of this technique is of $1\text{--}2\ \mu\text{m}$ only, it must not be ruled out that the errors in our assaying procedure arise, at least partially, due to application of EDS as reference methods.

Another problem is “matrix effect”. As indicated in Table 3, the elemental sensitivity factors exhibit variability for different gold alloys. In principle, this is known effect, mainly due to incongruent nature of vaporization and effusion (see, e.g., the results of vaporization of AlNi₃ alloy and pure Al and Ni presented in Ref. [28]). In the framework of our quantification approach it means that (i) every sort of the gold alloys should be properly calibrated before assaying and (ii) experimental conditions during the measurements of reference and determined samples should be identical. Fortunately, the number of the commercial gold alloys is limited. Besides 18 ct alloys studied in the present work, the low title alloys of 14 ct (583 wt.% of gold) and 8 ct (333 wt.%) are often used in goldsmithery, along with more rare 22 ct (917 wt.%) and 23 ct (958 wt.%) gold.

4. Summary

The present study provides a detailed characterization of vaporization of coinage metals and 18 ct gold alloys. The measurements were carried out by means of a high-temperature Knudsen effusion mass spectrometer equipped with a linear time-of-flight analyser and an electron impact ionization ion source. We performed the isotopic fractionation measurements in vapour phase and estimated the enthalpy of vaporization for pure Au, Ag and Cu.

Our purpose was to examine the applicability of a reasonably priced custom-built KEMS instrument for goldsmithery. The results of the present work show that it is possible to use Knudsen effusion mass spectrometry for gold determination but only with a proper calibration involving standard reference materials. At this stage, an accuracy of the gold assay with KEMS is of the same order or better as that of XRF, at least for basic ternary alloys, but our results are still inferior to cupellation. One of the most interesting characteristic of KEMS lies perhaps in the fact that it requires no special sample preparation beyond simple cleaning. In this respect, the method turns out to be more practical than EDS or XRF.

The following investigations and apparatus improvements are in progress or planned:

- (1) Quantification of other commercial gold alloys currently used for jewellery fabrication.
- (2) Involving more accurate reference methods for calibration of the standards.
- (3) Rearrangement of the instrument resulting in the vertical position of the effusion cell that should improve uniformity of

sample melting and vaporization and, in the long run, positively influences on the accuracy of assaying.

- (4) Increasing the sample-to-orifice squares ratio in the cell along with decreasing the temperature of assay that should guarantee true Knudsen effusion conditions (thermodynamic equilibrium).
- (5) Improvement the vapour-tightness of the effusion cell for avoiding uncontrolled loss of analysed materials during assaying.

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References

- [1] F.E. Beamish, J.C. Van Loon, *Recent Advances in the Analytical Chemistry of the Noble Metals*, Pergamon, Oxford, 1972.
- [2] A. Marucco, W. Stankiewicz, *Gold Technol. No. 24* (1998) 14.
- [3] V. Rößiger, B. Nensel, *Gold Bull.* 36 (2003) 125.
- [4] O. Senofonte, S. Caroli, *J. Anal. At. Spectrom.* 15 (2000) 869.
- [5] D.J. Kinneberg, S.R. Williams, D.P. Agarwal, *Gold Bull.* 31 (1998) 58.
- [6] M. Corsi, G. Cristoforetti, V. Palleschi, A. Salvetti, E. Tognoni, *Eur. Phys. J. D13* (2001) 373.
- [7] L.E. García-Ayuso, J. Amador-Hernández, J.M. Fernández-Romero, M.D. Luque de Castro, *Anal. Chim. Acta* 457 (2002) 247.
- [8] J.C. Van Loon, R.R. Barefoot, *Determination of the Precious Metals: Selected Instrumental Methods*, Wiley, Chichester, 1991.
- [9] M. Brill, *Gold Technol. No. 22* (1997) 10.
- [10] U. Bardi, S. Caporali, S.P. Chenakin, A. Lavacchi, E. Miorin, C. Pagura, A. Tolstogousov, *Surf. Coat. Technol.* 200 (2006) 2870.
- [11] S. Daolio, C. Pagura, A. Tolstogousov, *Appl. Surf. Sci.* 222 (2004) 166.
- [12] K. Hilpert, *Fresenius J. Anal. Chem.* 370 (2001) 471.
- [13] J. Drowart, C. Chatillon, J. Hastie, D. Bonnell, *Pure Appl. Chem.* 77 (2005) 683.
- [14] D.F. Avery, J. Cuthbert, N.J.D. Prosser, C. Silk, *J. Sci. Instrum.* 43 (1966) 436.
- [15] <http://www.kaesdorf.de>, 2008.
- [16] W.C. Wiley, I.H. McLaren, *Rev. Sci. Instrum.* 26 (1955) 1150.
- [17] <http://www.burle.com>, 2008.
- [18] <http://www.vts-createc.com>, 2008.
- [19] P. Clausing, *Ann. Physik.* 12 (1932) 961.
- [20] E.H. Kennard, *Kinetic Theory of Gases*, McGraw-Hill, New York, 1938.
- [21] <http://www.adixen.com>, 2008.
- [22] B.H. Wolf, in: B.H. Wolf (Ed.), *Handbook of Ion Sources*, CRC Press, Boca Raton, 1995, p. 331.
- [23] C.I. Whitman, *J. Chem. Phys.* 20 (1952) 161.
- [24] K.F. Herzfeld, E. Teller, *Phys. Rev.* 54 (1938) 912.
- [25] E. Fermi, *Thermodynamics*, Prentice-Hall, New York, 1937.
- [26] R.R. Hultgren, *Selected Values of the Thermodynamic Properties of the Elements*, Metals Park, OH, 1973.
- [27] M.W. Chase, Jr., *NIST-JANAF Thermochemical Tables*, 4th edition, *J. Phys. Chem. Ref. Data*, Monograph No. 9, 1998.
- [28] K. Hilpert, *Rapid Commun. Mass Spectrom.* 5 (1991) 175.
- [29] P. De Bièvre, P.D.P. Taylor, *Int. J. Mass Spectrom. Ion Proc.* 123 (1993) 149.