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Gold assay with Knudsen effusion mass spectrometry

Questa è la Versione finale referata (Post print/Accepted manuscript) della seguente pubblicazione:

Original Citation:

Gold assay with Knudsen effusion mass spectrometry / U. Bardi; F. Niccolai; M. Tosti; A. Tolstogouzov. - In: INTERNATIONAL JOURNAL OF MASS SPECTROMETRY. - ISSN 1387-3806. - STAMPA. - 273:(2008), pp. 138-144. [10.1016/j.ijms.2008.03.013]

Availability:

This version is available at: 2158/778983 since:

Published version:

DOI: 10.1016/j.ijms.2008.03.013

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Publisher copyright claim:

(Article begins on next page)

ARTICLE INFO

Article history:

Received 20 February 2008

Received in revised form 29 March 2008

Accepted 31 March 2008

Available online 8 April 2008

Keywords:

Knudsen effusion mass spectrometry

Assay

Jewellery alloy

Energy dispersive X-ray spectroscopy

Time-of-flight analyser

ABSTRACT

Commercial 18 carat (ct) gold alloys along with pure coinage metals have been analysed by Knudsen cell effusion mass spectrometry. Isotopic fractionation in vapour phase and the effect of sample size were estimated for Au, Ag and Cu samples. The assaying of the gold content was achieved by calibration with respect to standard reference alloys measured with energy dispersive X-ray fluorescence spectroscopy. The accuracy of the gold determination resulted of about 1.5 wt.% in the ternary system Au-Ag-Cu.

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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 analytical and instrumental techniques, applying to determination of gold content, the reader is addressed to the monograph of V. V. Korshak [8].

Energy dispersive X-ray fluorescence spectroscopy has gained most popularity now, finding service in both jewellery and assay laboratories. There are many producers of XRF analyzers on the market. According to Ref. [9], XRF can measure the content of an alloy with an accuracy of 0.75 wt.% under standard conditions, however typical accuracy is about 1 wt.% for non-destructive, determines all elements in the sample (C, B, Be), but only in the near-surface layer (up to 1 mm in depth). Electroplating or chemical treatment of the surface composition, distort the results of XRF measurements, the sample surface should be clean and flat, and at least 3 mm in diameter. Curved surfaces are not suitable since the emitted X-rays are randomly scattered.

Therefore, the development of novel methods for gold assay is still ongoing. Recently, SIMS and mass-resolved laser ionization mass spectrometry have been applied to the characterization of electrodeposited Au, Pd and Ru coatings [10], and to the analysis of gold coins [11]. These techniques are very sensitive, but the advantage of sputter depth profiling within the near-surface layer, however, they are scarcely suited for the determination of the bulk elemental content.

Knudsen (cell) effusion mass spectrometry has been proved to be a powerful tool for determination of the properties of different materials, including gold alloys.

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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. The optimal temperatures in our experiment coincided with T_1 , i.e., with the temperatures of 1 mbar vapour pressure of the pure component.

The best test for proper operation of a Knudsen cell is determination of the enthalpy of vaporization of a substance. The equation in chemical thermodynamics [25] relates the temperature to the change in the equilibrium constant of the reaction. It assumes that the enthalpy change is constant over the temperature range as

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

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

For a simple vaporization reaction like $\text{A}(\text{l}) \rightarrow \text{A}(\text{g})$, the equilibrium constant $K = p(\text{A})$, where p is the pressure of the vapor. For a Knudsen cell, $p(\text{A}) \propto I(\text{A}) \cdot T$ (for details see Ref. [26]), where I is the ion intensity of A-element, the temperature may be determined from the slope of $\ln(K)/T$ vs $1/T$. The reciprocal absolute temperature without known parameters. Conversely, these extra parameters can be determined in order to determine ΔS° .

The Van't Hoff plots for the main isotopes of copper and silver are shown in Fig. 5. The results of the ΔH° estimation at different temperatures of the measurements are presented in Table 2. They show that the values of ΔH° calculated at different temperatures using Ref. [26] and the currently accepted values for the vaporization of pure Cu, Ag and Au at room temperature are in good agreement. The discrepancy between our results and the literature values is interpreted as due to the fact that the sample in the Knudsen cell is not perfectly in equilibrium with the vapour. From the point of view. It is likely that an error is introduced by the modest value of the sample-to-orifice distance $s = 25\text{--}35$ (should be 10^2 , at least, according to

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 data
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 copper and silver as a function of relative temperature. The temperature of the effusion cell is indicated at the upper left corner of every panel.

Fig. 4. Isotopic fractionation $\delta^{65}\text{Cu}$ and $\delta^{109}\text{Ag}$ measured at different temperatures. The temperature of the effusion cell is indicated at the upper left corner of every panel.

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

determined for a LPT 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

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

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	
		<i>W</i>	<i>SF</i>	<i>W</i>	<i>SF</i>	<i>W</i>	<i>SF</i>	<i>W</i>	<i>SF</i>
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	–	–

Fig. 6. Peak intensity of the main isotopes of Cu, Ag, Au, Zn temperature measured under vaporization of the common Alloy 2R (b) and Alloy 3R (c). The temperature of the effusion range.

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

13 wt.% for the quaternary alloys. For Ag accuracy of determination within 25 wt.% 3 wt.%. Since EDS also needs adequate calibration depth of this technique is of 1–2 μm only, that the errors in our assaying procedure due to application of EDS as reference method.

Another problem is “matrix effect”. As elemental sensitivity factors exhibit variations in alloys. In principle, this is known effect, matrix nature of vaporization and effusion (see, e.g., vaporization of AlNi₃ alloy and pure Al and Ni present in the framework of our quantification approach). (i) sort of the gold alloys should be properly calibrated and (ii) experimental conditions during the analysis of the determined samples should be identical. The number of the commercial gold alloys is limited. In the present work, the low title (18 ct (75 wt.% of gold) and 8 ct (333 wt.%) are often used in the jewelry with more rare 22 ct (917 wt.%) and 23 ct (1000 wt.%)

4. Summary

The present study provides a detailed characterization of coinage metals and 18 ct gold alloys. The experiments were carried out by means of a high-temperature mass spectrometer equipped with a linear ion optics and an electron impact ionization ion source. The results of the isotopic fractionation measurements in vaporization of the enthalpy of vaporization for pure Au, Ag, Cu, Ni, and Zn.

Our purpose was to examine the applicability of the custom-built KEMS instrument for gold assay. The results of the present work show that it is possible to perform mass spectrometry for gold determination. For proper calibration involving standard reference materials, an accuracy of the gold assay with KEMS is of the order or better as that of XRF, at least for 18 ct gold alloys, but our results are still inferior to cupellation. An interesting characteristic of KEMS lies in that it does not require no special sample preparation before analysis. In this respect, the method turns out to be more convenient than XRF.

The following investigations and applications are in progress or planned:

- (1) Quantification of other commercial gold alloys for jewellery fabrication.
- (2) Involving more accurate reference materials for the standards.
- (3) Rearrangement of the instrument resulting in the modification of the effusion cell that should

giam for his assistance in the development and assembling of the instrument, and Dr. S. Kaesdorf advising us about adjustment and optimization of LFT 10 analyser. Our thanks go to Dr. M. Caneschi for the gold alloys presented to our measurements. Also we would like to thank Mr. M. Stancampiano and Mr. R. Stancampiano, of the E. Stancampiano s.p.a. company, for their interest and support of this work. Finally, we are much obliged to the (unknown) reviewers who helped us to amend our presentation.

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