The determination of the content of gold and silver in geological samples

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A method has been elaborated for the determination of the content of gold and silver in geological samples by atomic absorption spectrophotometry (AAS) in combination with the fire assay method. The weight of sample used for analysis was 10 g. Sulphur present as sulphide, which is an undesirable element in smelting, was removed by the addition of iron to the charge. The sample was smelted with fluxes and lead oxide to replace the silver and gold by lead and to transfer non-precious elements to slag. Lead was separated from precious metals by cupellation. The separated silver and gold alloy was dissolved with aqua regia with addition of hydrochloric acid in excess. Silver and gold were determined from the same solution. For determination of the silver content, the AAS method with an air-acetylene flame was used. Gold was determined in a graphite furnace with the addition of a matrix modifier in an argon current, at an atomization temperature of $t = 2200$ ºC. The lower determination limit for silver was 0.05 g/t and for gold 0.005 g/t. The results of the analysis for silver and gold obtained with the proposed method showed good agreement with the results of the analysis of the same samples with the fire assay method.

Keywords: geological sample, gold, silver, fire assay, atomic absorption, air-acetylene flame, graphite furnace.

INTRODUCTION

Gold occurs in small quantities in clays, pyrite and in almost all silver, copper, bismuth, lead, zinc, tellurium and antimony ores.

Due to the very heterogeneous composition of geological samples and the low gold and silver contents, irrespective of the analytical method applied, their determination proceeds in two stages. The first stage comprises the separation of gold and silver from the non-precious portion of ore and the second stage comprises the determination of the content of the separated silver and gold.

The fire assay method is the oldest and most reliable method used for the concurrent determination of silver and gold in all gold-bearing materials. Apart from this method, other methods for the determination of silver and gold have been published.

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One of the known procedures is the extraction of gold with methyl isobutyl ketone (MIBK)[1–3,10] and its direct determination by flame atomic absorption spectropho-tometry. Graphite furnace atomic absorption spectrophotometry (GFAAS) enables the detection of low concentrations of silver and gold, but previous extraction of the precious metals is required before their determination. Kontas[4] has indicated that it is possible to avoid the application of organic solvents for the extraction of gold, the gold is reduced with stannous chloride and then the gold is amalgamated with mercury. The usage of a small sample weight (1 g) limits the application of this method, while increasing the sample weight to 10 g extends the analysis time. A prerequisite of the analysis of arsenic–antimony ores by complete extraction of the gold with MIBK[5] and its determination in a graphite furnace is the previous precipitation of iron, with ammonium hydroxide, in order to eliminate interferences in the recording of gold. Moloughney[6] used multiple scorification with the aim of reducing the quan-tity of to decrease lead required to extract the silver and gold from the sample. Silver and gold separated from this alloy by acidic dissolution and separately analyzed by flame AAS. The results of the analysis of silver and gold using inductively coupled plasma–mass spectrometry (ICP-MS)[7] in combination with the fire assay method were compared with the results obtained by GFAAS and with the results obtained by inductively coupled plasma atomic emission spectrometry (ICP-AES). But only with the GFAAS and ICP-MS techniques was it posible to determine lower contents of gold in the analyzed samples.

The fire assay method, as the oldest and the most accurate method for the deter-mination of low contents of silver and gold is a long, tedious and expensive process. Our new investigations have been proceeding in the direction of the determination of the silver and gold content by methods which are more economical, which use less time and provide good reproducibility of results. One of the trials was the direct determina-tion of the gold content by the GFAAS method in plageo-granite.[9] The sample weight was 0.1 and 0.25 g and the sample was dissolved in a teflon vessel by mineral acids. The results of the investigations showed that the determination detection limit was 1 g/t Au. The large standard deviation obtained was the result of the non-homogenous distribu-tion of gold in the sample.

In this work, the investigations encompassed the selection of the sample weight, the manner of removal of interfering elements and the establishment of the accuracy of the obtained results for gold and silver as related to the fire assay method. In the first stage, the fire assay method was used for the pre-concentration of the gold and silver from a 10 g sample. In the sample smelting procedure with the addition of fluxes, the precious metals present were extracted with lead and the oxides of the non-precious metals were transferred to slag. By cupellation in the oxidation me-dium, lead was separated from the gold and silver, so at the end of the process, a bead containing the gold and silver remained. The obtained bead was dissolved with aqua regia containing additional hydrochloric acid in excess and the gold and silver content was immediately determined from the same solution. The gold content was deter-mined by AAS in a graphite furnace and the silver content was determined by air-acetylene flame AAS.

EXPERIMENTAL

Reagents

Charge for smelting: PbO, Na_2CO_3, $Na_2B_4O_7$, flour and iron.

Acids: HF; HNO_3, diluted (1:1); aqua regia; HCl.

Standard gold and silver solutions: Commercial solutions for AAS of 1000 g/cm³.

Solutions for the establishment of the calibration curve for gold were always prepared fresh on the day when recording the determination was to be performed.

Gold matrix modifier: 0.05 mg Ni for 5 l. Water solution $Ni(NO_3)_2 \cdot 6H_2O$.

All the chemicals used were of analytical grade purity. The solutions were prepared with double-distilled water.

Apparatus

Fire-resistant crucibles of 150 cm³, iron cups, cupels 60 mm, shaft furnace with an operating temperature of 1070–1100 ºC, cupellation furnace of 20 kW.

A flame atomic absorption spectrophotometer and an atomic absorption spectrophotometer with a graphite furnace, autosampler and printer.

Hollow cathode lamps for silver and gold. L'vov platforms and tubes.

Micropipettes.

Procedure

Selection of optimal sample weight. The selection of the optimal sample weight was preceded by a trial of the acidic dissolution of 10 g geological samples.

For the combined method described in this paper, investigations of the influence of various sample weights (2.5; 5; 10; 15 and 25 g) on the silver and gold results were made, in order to select the optimal sample weights (Table II).

Smelting and cupellation process. For the combined method of fire assay and AAS, a sample weight of 10 g was selected. For the removal of sulphur, which in the smelting process affects the loss of precious metals, two procedures were applied. In the first procedure samples were roasted at a temperature of 600 ºC for a duration of two hours and in the second iron was added to smelting charge. The charge components were the following: lead oxide (20 g), sodium carbonate (25 g), sodium tetraborate (15 g) and reducing reagent – flour (5 g). The charges prepared in such a manner were previously well mixed with the samples from both processes and quantitatively transferred to fire-resistant crucibles. The smelting process was performed at the temperature of 1070 ºC for a duration of 1 h. The smelted material was tapped into iron cups. After cooling, the lead with precious metals was separated from the slag by forging, placed into heated cupels and cupellated at a temperature between 890–940 ºC in duration of 20–30 minutes. The separated bead retained at the bottom of the cupel was dissolved with acids in the next procedure.

Dissolution of the bead. The obtained silver and gold alloy bead, was dissolved with 2 cm³ 50 % (v/v) nitric acid and then with 2 cm³ of aqua regia. To obtain silver in the form of complex compounds $AgCl_2^-$ and $AgCl_3^{2-}$, the solution was treated with 25 % (v/v) hydrochloric acid[1] in a 100 cm³ volumetric flask. A sample blank was prepared in the same manner and with the same quantity of reagents, only without the analyzed sample.

Silver determination. All the investigations were performed using a AAS Perkin Elmer M-403 atomic absorption spectrometer. The solutions for the calibration curve (1, 2, 3, 4 and 5 g Ag/cm³), the sample blank and the dissolved samples were introduced into the air-acetylene flame and the silver recorded at the wavelength of 328.1 nm with a slit of 0.7 nm. All the dissolved samples were determined immediately after filling the volumetric flask, and corrected for the silver content of the lead oxide (sample blank).

Gold determination. All gold determinations were performed using Perkin Elmer 1100B AAS with a graphite furnace, HGA (high graphite atomization) 700. The samples were charged into the

tube with an autosampler AS-70 on the L'vov platform. The solutions for the establishment of the calibration curve (20, 40, 60 and 80 ng Au/cm^3) were prepared using a nickel matrix modifier in an argon current. To obtain good signals for gold, a graphite furnace was selected with a temperature stabilized platform - STPF.[8] A stabilized temperature platform furnace is not a piece of hardware but a new concept that makes proper use of the existing equipment to reduce inteferences to an absolute minimum. It includes the following feature:

a) Maximum power heating,

b) Atomization off the L'vov platform,

c) A minimal temperature difference of 1000 ºC between thermal pretreatment and atomization,

d) Use of matrix modifiers,

e) Gas stop during atomization,

f) Peak area integration.

In case when all the above features were applied, very frequently a negative value for the zero standard was obtained, so that for the determination of the gold concentration, the method of peak height measurement was selected. The use of an autosampler is necessary for a series of samples. The selected instrumental conditions were: wavelength 242.8 nm, slit 0.7 nm; lamp current 10 mA; integration time 5 s.

Of all parameters for the determination of gold by AAS with a graphite furnace, the most important are the regime of furnace heating, time ramp and hold time temperature, as well as gas flow rate. The optimal conditions are given in Table I. Using these conditions, the calibration curve shown in Fig. 1 was obtained after background correction.

TABLE I. HGA conditions for the determination of gold

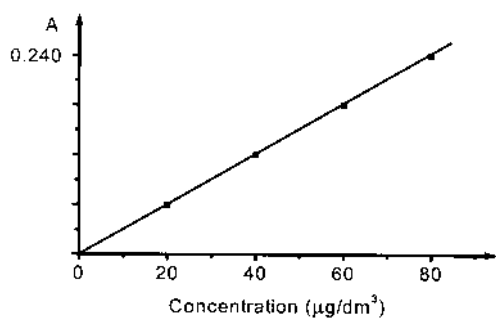| Step number	Furnace temperature/ºC	Time ramp/s	Hold time/s	Internal gas flow cm^3/min
1	120	10	10	300
2	1000	10	25	300
3	2200	0	3	0
4	2650	1	3	300

Fig. 1. Calibration curve for gold using a graphite furnace.

For the measurements, 10 ℓ of standard or sample solution and 5 ℓ of matrix modifier were automatically pipetted onto the plattform.

RESULTS AND DISCUSSION

The experimental investigations were preceded by a trial of the direct determination of gold in geological sample by GFAAS, without the previous separation of gold from the non-precious components of the sample. The sample was dissolved with acid in a Teflon vessel, the destruction of the silicate structure being achieved with HF. The gold content was determined by GFAAS and results compared with the results of the analysis of the same sample by the fire assay method. Lower values were obtained by the GFAAS method, which showed that in the direct determination of gold a high background and irregular peaks were obtained as disturbances due to the presence of non-precious components (especially iron)[5] in the sample.

Due to the well-known fact that gold occurs in nature in quartz veins, it is non-homogenously distributed in gold ores. Hence, according to our the experience and the experience of other authors,[1–3,5] a minimum sample weight of 10 g is considered necessary to overcoming this problem.

The investigations were performed on one composite geological sample for which mean values of the silver (1.7 g/t) and gold (0.32 g/t) had previously been determined by the fire assay method. Dissolution of 10 g of sample were performed in two different manners: using acids and by the fire assay. The acidic dissolution time was 12 h, using a larger quantity of acid and separation of the salts, which are undesirable in the further procedure.

The application of the fire assay method in the first stage of the separation of precious metals enabled the complete destruction of the sample structure and the complete separation of the silver and gold from the non-precious components of the sample. The total duration of this dissolution method, which includes taking into consideration the smelting, and cupellation processes and the acidic dissolution of the bead of silver and gold, was 2.5 h, which is significantly shorter than the 12 h required for the acidic dissolution of the sample.

The optimal sample weight of 10 g was confirmed after investigation of the influence of various sample weights on the gold and silver results. The result of the analysis for the silver and gold content by the proposed combined method using five different sample weights of the same geological sample are presented in Table II.

TABLE II. Results of the analysis of different sample weights of the same geological sample

Weight/g	Ag/g t^{-1}	Au/ g t^{-1}
2.5	0.6	0.15
5	1.0	0.27
10	1.8	0.33
15	1.1	0.30
25	1.5	0.31

By comparison of the results of the analysis of the different sample weights by the combined method, with the results of analysis by the fire assay method (Ag = 1.7 g/t and Au = 0.32 g/t), it may be observed that sample weights less than 10 g lead to a decrease in the found values for the silver and gold content but that the results obtained using a sample weight of 10 g are close to the results obtained by the classical fire assay method (where a sample weight of 100 g provides high accuracy of the analysis for Ag and Au).

The presence of sulphur in the form of sulphides in the ore, is unfavorable in the smelting process since it causes precious metals losses due to poor separation of the slag from the metal. Accordingly, the sulphur was removed in two manners: by roasting at 600 ºC and by the addition of iron to the charge, which reacts with sulphur and fluxes and transfers it into the slag. Tables III and IV presenents the results of the determination of silver and gold by AAS after application of the above-mentioned sulphus removal procedures. It may be concluded that the results, obtained after sulphur removal by direct smelting with iron, are better than those obtained after sulphur removal by roasting.

After sample smelting, the slags were analysed for silver and gold by the combination of the fire assay and the AAS methods, to establish eventual losses the content of silver and gold in the slags were below the lower detection limit of this method.

TABLE III. The determined content of Ag and Au in the samples after removal of sulphur by roasting

Ser. No.	Ag/g t^{-1}	Au/g t^{-1}
1	0.5	0.34
2	2.2	0.38
3	3.2	0.40
4	0.5	0.40
5	1.2	0.34
6	0.5	0.27
7	0	0.24
8	1.0	0.33
9	1.2	0.30
10	1.3	0.30
11	0.5	0.29
Statistics	$x = 1.1$	$x = 0.33$
	$s = 0.9132$	$s = 0.0524$
	$RSD = 83\ \%$	$RSD = 16.0\ \%$

TABLE IV. The determined content of Ag and Au in the samples after removal of sulphur by the smelting process

Ser. No.	Ag/g t^{-1}	Au/g t^{-1}
I	1.9	0.27
II	1.0	0.25
III	1.0	0.35
IV	1.3	0.32
V	1.5	0.31
VI	1.5	0.33
VII	1.2	0.29
VIII	1.3	0.30
IX	1.0	0.31
X	1.9	0.34
XI	1.2	0.32
Statistics	$x = 1.3$	$x = 0.31$
	$s = 0.3267$	$s = 0.0290$
	$RSD = 25\ \%$	$RSD = 9\ \%$

Samples of different chemical compositions from different geological localities were analyzed in triplicate by both the decribed method and the fire assay (FA) method. The mean values of the found silver and gold contents are presented in Table V. The samples included copper ores (samples 1 to 4), gold ores-plageo-granites (samples 5 to 7) and poly-metalic ores (samples 8 to 10). The results show mutual agreement.

Comparing the results obtained by the combined method (Table IV) with the results of the fire assay method, good agreement may be observed for gold, while the silver values show larger deviations, but within a range which is satisfactory for the analysis of geological samples. Comparative results obtained using the two methods for the analysis of different samples (Table V) show small mutual deviation, which means that the accuracy of the results obtained by application of the combined method of fire assay and AAS can be considered as satisfactory.

TABLE V. Comparative results of the determination of the silver and gold content in g/t in geological samples by the combined method of FA/AAS and by FA method

Sr. No.	Sample	FA/AAS		FA		Ag	Au
		Ag	Au	Ag	Au		
1	Copper ore 1	0.8	0.23	0.6	0.20	0.2	0.03
2	Copper ore 2	2.3	0.27	3.0	0.25	0.7	0.02
3	Copper ore 3	2.0	0.51	2.3	0.62	0.3	0.11
4	Copper ore 4	1.5	0.08	1.2	0.10	0.3	0.02
5	Gold ore 1	4.5	9.50	5.4	8.90	0.9	0.60
6	Gold ore 2	4.2	1.44	3.5	1.54	0.7	0.10
7	Gold ore 3	2.7	0.34	3.0	0.34	0.3	0.00
8	PMO 1	2.0	0.28	1.5	0.35	0.5	0.07
9	PMO 2	6.4	0.96	5.6	0.80	0.8	0.16
10	PMO 3	0.6	0.05	0.4	0.05	0.2	0.00

However, in the same time interval, four times as many geological samples can be prepared for analysis for gold and silver by the above described method than for analysis by the classical fire assay method. By exclusion of sample roasting, using small fire-resistant pots (150 cm^3), using ten time less quantity of charge as compared to the classical fire assay method, using small cupels and shortening the duration times of all necessary operations, a more economical procedure has been developed for the quick and accurate control of the silver and gold content of geological samples.

CONCLUSION

A method has been elaborated for the quick and sufficiently accurate determination of the gold and silver content of geological samples. The precious metals are first separated from the total sample mass by the fire assay method. In this maner, the gold and silver are separated from interfering elements and concurrently concentrated, which enables the methods of flame atomic absorption spectroscopy and graphite furnace atomic absorption spectroscopy to be problemless applied for the determination of the content of gold and silver in geological samples.

И З В О Д

ОДРЕЂИВАЊЕ ЗЛАТА И СРЕБРА У ГЕОЛОШКИМ УЗОРЦИМА

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Разрађена је метода за брзо и тачно одређивање сребра и злата у геолошким узорцима атомском апсорпционом спектрофотометријом у комбинацији са купелацијом. Испитивања су обухватила: избор одваге, начин уклањања интерферирајућих елемената и утврђивање тачности добијених резултата сребра и злата у односу на методу купелације. За анализу је коришћена одвага 10 g узорка. Методом купелације брзо и ефикасно издвојени су племенити метали од укупне масе чиме су постигнута два важна ефекта. Злато и сребро одвојени су од интеферирајућих елемената и исто-

времено концентрисани, што је омогућило да се одређивање њихових садржаја методом AAS у пламену и графитној пећи обави без сметњи. Доња граница одређивања за сребро је 0,05 g/t а за злато 0,005 g/t. Резултати одређивања сребра и злата предложеном методом упоређивани су са резултатима анализе истих узорака класичном методом купелације, која користи одвагу од 100 g и показали су добро слагање. У поређењу са купелацијом разрађена метода скраћује време и смањује трошкове израде анализе.

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