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DETERMINATION OF GOLD IN GEOLOGICAL MATERIALS BY ATOMIC SPECTROSCOPY METHODS AFTER ENRICHMENT ON ION EXCHANGERS

(Figs. 2, Tabs. 6)

Abstract: Owing to low contents of gold in majority of geological materials, procedure of its determination by OES and AAS after preliminary enrichment using ion exchangers has been worked out. Conditions of two preconcentration procedures using strongly basic anion exchanger have been studied and their efficiency has been compared with extraction procedure. Reliability of the results obtained by proposed analytical procedures has been examined, whereby OES method with excitation in electric arc shows advantageous metrological and economical parameters. Using OES, determination limit of 0.001 ppm Au has been obtained when inweight of the sample is 5 g.

Резюме: Ввиду низких содержаний золота в большинстве геологических материалов был разработан метод его определения при помощи ОЭС и ААС после предварительного набогащения используя ионнообменную смолу. Были изучены условия двух приемов набогащения применяя сильно основные аниониты и их мощность сравнивалась с экстракцией. Была исследована точность результатов полученных предложенными аналитическими методами, причем метод ОЭС с возбуждением в электрической дуге обнаруживает выгодные метрологические и экономические параметры. Применяя ОЭС, при навеске пробы 5 г был получен лимит определения 0,001 г/т Au.

Introduction

According to Vinogradov (1962), contents of gold in majority of geological materials are present in clark concentrations. Its average content in the Earth's crust is $4.3 \, . \, 10^{-7}$ % ($5 \, . \, 10^{-7}$ % in ultrabasic rocks, $4 \, . \, 10^{-7}$ % in basic rocks, $4.5 \, . \, 10^{-7}$ % in granitoid rocks). Average contents of gold in meteorites, minerals and rocks, as well as forms of its occurrence and geochemical conditions of gold-bearing regions evolution are presented by Shcherbakov — Perezhogin (1964). Geochemical study of gold is dealt with also by Vincent — Crocket (1960) and its distribution — by Sighinolfi — Gorgoni (1977).

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Owing to the most frequent, relatively low contents of gold in various types of raw materials, its determination requires application of analytical methods characterized by high detectability, but also in these cases its preliminary enrichment is needed. At the same time, its distribution in rocks and minerals, as well as form of its occurrence should be taken into consideration. Tedious and cumbersome gravimetric method with fire-assay enrichment which has been until lately the most applied method in our country has been gradually replaced by more efficient methods, such as neutron activation, atomic absorption spectrometry, spectrochemical analysis, ICP, stripping voltammetry, spectrophotometry, etc. Among the given methods only the neutron activation analysis does not require preliminary chemical enrichment of gold.

At determination of gold by atomic absorption method which belongs to the most used ones at present, extraction of its chloride auri complex in methyl isobutyl ketone (Sighinolfi — Santos, 1976; Streško, 1979, and others) or dibutyl sulphide in toluene (Rubeška et al., 1977; Cambel et al., 1980; Branch — Hutchison, 1986, and others) is most often used in enrichment processes. Survey determination of gold in raw materials by atomic absorption using extraction agents is dealt with also by Weiss et al. (1975). Determination of gold in geological materials using AAS with flame and electrothermal atomization after its extraction with n-dibutyl sulphide in toluene is described by Weiss et al. (1983). Au contents can be generally determined by means of above-mentioned methods from $2 . 10^{-7}$ %. Determination of low Au contents (ppb) by atomic absorption spectrometry with flame and electrothermal atomization after extraction of bromide auri complex in amyl acetate is described by Haddon — Panthony (1980) and using coprecipitation with Hg by Kontas (1981).

Extraction enrichment, e.g. in form of gold carbonates in chloroform is also used for its spectrochemical analysis. Organic phase containing enriched gold is evaporated at presence of collector (e.g. graphite powder) as presented by Byrko et al. (1976). Vorobyova et al. (1974) determine gold in a similar way using diphenylthiourea in acetone for extraction. Tarasova et al. (1974) and Khitrov et al. (1980) used ion exchangers for preconcentration of gold from decomposed sulphide and sillicate samples. After ignition and mixing with graphite powder the samples were sprinkled into arc discharge. Using this procedure, the authors obtained precision of determination of ± 15 % and limit of determination of 0.01 ppm. Savinova et al. (1983) used polymer of thioether as a sorbent for spectrochemical determination of gold and platinum metals.

In the present work a procedure of determination of low gold contents in geological materials after its preliminary enrichment on ion exchangers was worked out. This excludes work of organic extraction agents, as they may have in some cases negative influence on working environment.

Experimental

The samples from various types of silicate rocks with gold contents determined by other independent analytical procedures or certified were analyzed in order to work out methodic procedure using atomic absorption spectrometry (AAS) and optical emission spectroscopy (OES).

Preparation of samples:

Owing to the possibilities of simultaneous determination of platinum metals, various, generally used decompositions by acids (HF + $HClO_4$, HBr + Br, aqua regia) as well as by addition of reduction agents (metallic Sn, solution of $SnCl_2$) were tested. Availibility of individual types of strongly basic anion exchangers was studied. ANKB-15 (U.S.S.R.) and Amberlite IRA-400 (U.S.A.) were applied. The latter seemed to be the most suitable regarding its higher exchange capacity (2.5 mmol/g).

On the basis of the obtained results (Medveď et al., 1985), the following preconcentration procedure was found as the most suitable for determination of gold:

5—10 g of sample are mixed with 2—4 g of NH_4NO_3 in a porcelain crucible and it is gradually heated until evolution of gases and oxidation of sample are finished. The crucible is then heated at 600—650 °C for 30 min. in a furnace. After cooling, the sample is transferred to a beaker (it is broken up with glass rod if necessary) and 0.5—1 g of NaCl are added to stabilize chloride auri complex in the solution. 30 ml of HCl and after 10—15 min. 10 ml of HNO_3 are gradually added to the mixture. After finishing of nitrogen oxides evolution, the solution is carefully boiled for 20 min. and evaporated on water bath to wet salts (not to dryness). Cal. 100 ml of 3 mol/l HCl (according to volume of centrifuge vessel) are added to wet salts and after their dissolution by boiling, non-decomposed residue is centrifuged at 4000—4500 rot./min. for ca. 10 min. Pure solution is poured out and the residue in the vessel is centrifuged again after its mixing with 3 mol/l HCl. 0.15 g of Amberlite IRA-400 are added to the joint solutions (ca. 150 ml). After 2—3 hour treatment on water bath at max. temperature of 75 °C, gold is separated from the solution.

In the case of determination of gold by AAS method (or OES-ICP) the following procedures may be applied:

A. Decanted anion exchanger is oxidationally burnt at max. temperature of 500 °C, the residue is dissolved in 8 ml of aqua regia and completed with water to 25 ml.

B. Decanted anion exchanger is eluted twice with 10 ml of 5 % thiourea in 0.01 mol/l HCl.

In order to verify the above procedures using ion exchangers, gold was determined after preconcentration by another method. After decomposition, the sample was completed to 100 ml and gold was extracted by 10 ml of isoamyl alcohol (Bazhov et al., 1976). Iron was reextracted in 0.1 mol/l HCl and gold was determined in organic solvent.

At spectrochemical determination of gold, besides ion exchanger, 0.05 g of spectrally pure graphite powder are added ot the joint centrifuged solutions before filtration (SU 602 Elektrokarbon Topoľčany). After filtration, the residue is thoroughly washed with 1 % HCl, filter is burnt and ignited for 1 hour at 500 °C.

Conditions of analysis:

Atomic absorption spectrometry

Atomic absorption spectrophotometer AA 875 Varian was used for determination of gold by AAS method. Hollow cathode lamp worked with the current of 4 mA. Measurements were carried out at wavelenght of 242.8 nm using deuterium background corrector. Halfwidth of spectral interval was 0.5 nm. Gas flows: air — 15 l/min.; acetylene — 1.5 l/min. (at atomization with isoamyl alcohol) and 2.5 l/min. (at atomization from water solution).

Basic solution of gold containing 1 mg of Au/ml was prepared by dissolving of 0.1 g of metal in 10 ml of warm aqua regia. The obtained solution was evaporated on water bath almost until dry and the residue was dissolved in 2 mol/l HCl and completed with the same acid to 100 ml. The solutions were further prepared by dilution or by another treatment according to corresponding working procedure.

Optical emission spectroscopy

In order to establish the conditions of spectrochemical determination of gold using D.C. arc, optimum exposure time of 120 s was determined by method of normalized evaporation relation curves (Plško, 1964).

On the basis of spectrochemical similarity with gold, cobalt and germanium were tested as reference elements and gallium trioxide, lithium carbonate, lithium fluoride, sodium chloride and potassium carbonate as spectrochemical additives.

The course of normalized evaporation relation curves (Fig. 1) shows that gallium trioxide proved to be the most suitable spectrochemical additive. Better simultaneous evaporation was reached when cobalt was used as a reference element.

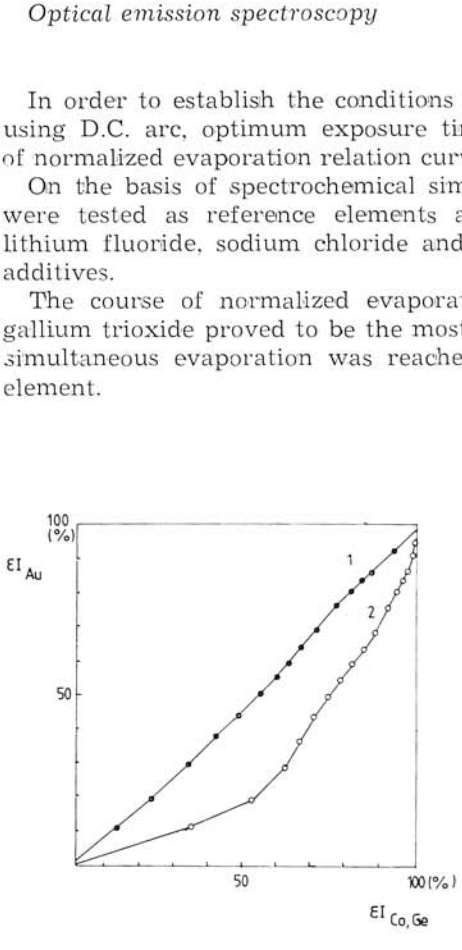

Fig. 1. Normalized evaporation relation curves for spectral lines: 1 – Au 267.591 nm Co 252.136 nm; 2 – Au 267.591 nm Ge 265.117 nm.

On the basis of the achieved results, 0.01 g of Ga_2O_3 with additive of 0.1 % of Co_3O_4 is added to the residue after ignition of ion exchanger with graphite powder and the mixture is homogenized and used for spectrochemical analysis.

Spectra of samples and of calibration standards prepared in the same way using solutions of gold with the known concentrations were analyzed spectrographically under the conditions given in Tab. 1.

Measured blackening values of gold spectral lines of 267.59 nm and of the corresponding background, as well as of cobalt spectral line of 252.13 nm are transformed to Y values (log I) by means of emulsion calibration curve for the area of 250 nm. Analytical calibration curve is plotted in coordinates ΔY versus log C (Fig. 2).

Table 1

Conditions of spectrochemical determination of gold

Spectrograph	PGS-2
Spectral range	210—390 nm ($\alpha = 5.65$), m = 1
Intermediate diaphragm	3.2 mm
Slit width	0.020 mm
Kind of illumination	three-lens with intermediate stop
Electrode material	graphite, Elektrokarbon Topoľčany
Sample bearing electrode	SU-308
Counter electrode	SG-359
Electrode gap	3 mm
Kind of emulsion	ORWO WU 3
Developer	ORWO R 09 (dil. 1 : 20)
Kind of excitation	D.C. arc, anodic polarization of sample bearing electrode
Voltage	220 V
Current	6 A
Exposure time	120 s
Photometer	MD — 100
Spectrochemical additive	Ga_2O_3
Line of analyzed element	267.59 nm Au
Line of reference element	252.13 nm Co

Table 2

Results of determination of gold in geological materials by AAS method after its preconcentration by extraction in isoamyl alcohol and by ion exchanger (A method)

Sample No.	Extraction ppm	A method ppm	Sample No.	Extraction ppm	A method ppm
1	30.5	29.0	13	0.9	1.1
2	2.0	1.9	14	5.5	6.3
3	8.5	8.9	15	0.3	0.6
4	6.3	5.9	16	3.4	4.2
5	1.9	2.4	17	6.6	7.6
6	6.8	5.6	18	3.3	2.9
7	2.3	2.6	19	1.6	1.7
8	5.2	5.0	20	6.8	6.0
9	4.4	4.3	21	1.8	2.4
10	4.4	5.2	22	6.0	5.6
11	0.8	1.0	23	2.3	2.6
12	2.7	3.2	24	1.8	1.7

Results and discussion

Comparison of the results of gold determination by AAS method after its extraction enrichment with the results obtained by enrichment in accordance with A method is listed in Tab. 2 and in accordance with B method in Tab. 3.

Table 3

Results of determination of gold in geological materials by AAS method after its preconcentration by extraction in isoamyl alcohol and by ion exchanger (B method)

Sample No.	Extraction ppm	B method ppm	Sample No.	Extraction ppm	B method ppm
25	2.19	2.30	30	0.34	0.20
26	3.06	2.95	31	1.70	1.75
27	4.27	4.35	32	1.00	1.08
28	2.14	2.35	33	1.02	1.13
29	1.89	1.75	34	0.20	0.12

Table 4

Statistical evaluation of dependence of results obatined after extraction on results with the use of ion exchangers

	A method	B method
Correlation coefficient	0.993	0.992
Orthogonal regression coefficient	0.942	1.004

Table 5

Gold contents determined in standard sample JAM E-19

x_{1-6}	2.03; 2.19; 2.03; 1.75; 2.00; 1.75
x_{rv}	2.00 ± 0.25
$\bar{x}$	1.96
s_r	8.9 %
s	0.17

Explanations: x_{1-6} – repeated determinations (ppm); x_{rv} – recommended value (ppm); $\bar{x}$ – arithmetical mean (ppm); s – standard deviation (ppm); s_r – relative standard deviation (%).

Correlation coefficients (r) and orthogonal regression coefficients (W_{ort}) of the results of analysis after enrichment on ion exchangers in dependence on the results obtained after extraction enrichment (Tab. 4) were calculated by means of procedure described by Holdt (1964). Covariance necessary for calculation of the given values is determined according to Plško — Florián (1980).

As it results from the data given in Tab. 4, correlation and orthogonal regression coefficients do not significantly differ from one in the both cases. This fact proves a good agreement of the results obtained by described preconcentration procedures using AAS in the given concentration interval.

The reliability of the whole analytical procedure was also examined by repeated analysis of the standard sample JAM E-19 prepared by the Czech Geological Bureau and tested by round-robin analysis in 8 laboratories. Recommended value of gold content in this sample is 2.00 ± 0.25 ppm (Špačková et al., 1985).

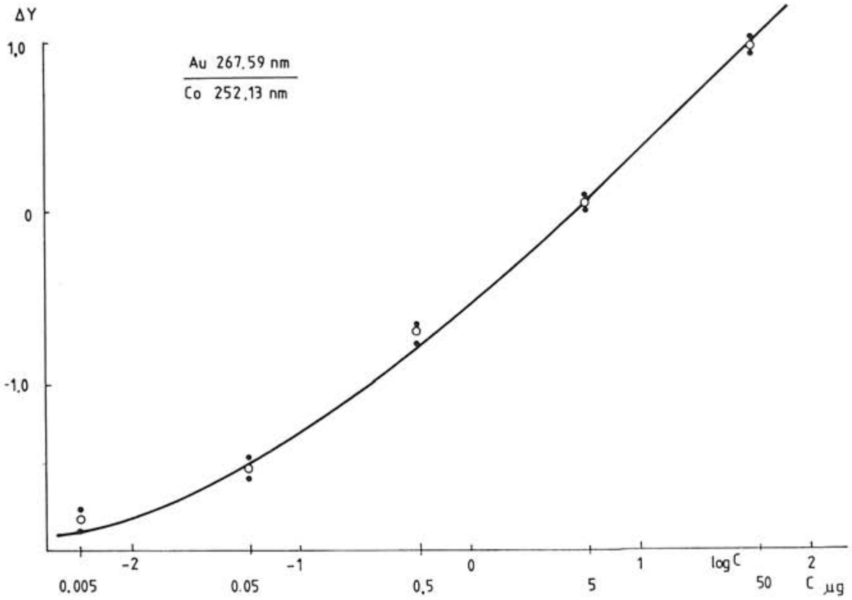

Fig. 2. Analytical calibration curve for determination of gold, spectral lines Au 267.59 nm Co 252.13 nm.

Results of repeated analyses using B method of enrichment with subsequent determination of gold by AAS are given in Tab. 5.

Agreement of average value with recommended value was examined by t-test. On the basis of experimental data t = 0.367 was obtained. Table value for degree of freedom f = 6 + 7 — 2 = 11 equals on probability level of 95 % to $t_{tab} = 2.201$ (Owen, 1966). On the basis of comparison of the obtained values it was proved that the used procedure provides accurate results not loaded by systematic error.

By means of described OES method, gold can be determined in the samples of geological materials in the range from 0.005 μg to 50 μg what corresponds to concentrations from 0.001 to 10 ppm when inweight of the sample is 5 g. In

Table 6

Comparison of results of gold contents in geological materials determined by different analytical methods in various laboratories

Sample	Laboratory and method of determination (contents are in ppm)			
	Present work	Geol. Survey Brno	CS. Uranium Survey Stráž. p. Ralskem	Certified reference materials
	OES	AAS	Neutron activation	Khitrov–Kortman (1974)
1	0.16	0.11		
2	0.46	0.40		
3	1.30	1.04		
4	1.80	1.62		
46	0.011		0.011	
68	0.460		0.427	
MIV-1	0.32			0.40
PIM-1	0.13			0.09
Ryžik	0.05			0.03
DIM-1	0.09			0.07

the case of determination of higher gold concentrations it is possible to use (after enrichment) the corresponding aliquot part.

From comparison of attainable limit of determination with average gold contents in geological materials, as mentioned in the introduction, good applicability of the proposed procedure to analysis of these contents can be stated.

Samples with known gold content as well as certiifed reference materials were used for examination of reliability of analytical results (Khitrov—Kortman, 1974). Gold contents were determined gravimetrically in the given samples after fire-assay enrichment, by AAS method after preconcentration by means of isobutyl ketone or dibutyl sulphide and by neutron activation.

Owing to very low gold contents in the analyzed rocks lying at the level of tenth to hundreth of ppm, a good agreement of our results with the values given in Tab. 6 was obtained by the above procedure. In the given concentration area it corresponds to hitherto achieved experience with determination of gold carried out after preliminary extraction enrichment by AAS method.

Accuracy of spectrochemical determination established from repeated measurements is characterized by relative standard deviation of 7 %.

On the basis of obtained results and operational safety of work it can be stated that spectrochemical determination of gold after its preconcentration on ion exchangers, i.e. without use of organic solvents, represents well applicable method of determination of this economically specially significant element characterized by sufficient detection limit as well as by reliability of achieved results, whereby requirements concerning economic parameters are fulfilled too.

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REFERENCES

BAZHOV, A. S. — SOKOLOVA, E. A. — SHCHERBOV, D. P., 1976: Ekstrakcionno-atomno-absorbcionnoe opredelenie zolota pri nizkom soderžanii v geologičeskich objektach. Ž. anat. chim. (Moscow), XXXI, 6, pp. 1098—1103.

BRANCH, CH. H. — HUTCHISON, D., 1986: Comparison between methyl isobutyl ketone and diisobutyl ketone for the solvent extraction of gold and its determination in geological materials using atomic absorption spectrometry. Analyst (London), 111, pp. 231—233.

BYRKO, V. M. — BUSEV, A. I. MENANISHVILI. I. P., 1976: Ekstrakcionnoje koncentrirovanie Pd, Pt i Au 3,5 difenil-l-tiokarbamidopirazolinom i ich opredelenije v polimetalličeskich rudach i sulfidnych koncentratach. Atomno-absarbcion. analiz prom. materialov i syrja. (Moscow) pp. 151—155.

CAMBEL, B. — STREŠKO, V. — ŠKERENČÁKOVÁ, O., 1980: The contents of gold in pyrites of various genesis. Geol. Zbor. Geol. carpath. (Bratislava) 31, 1—2, pp. 139—159.

HOLDT, G., 1984: Der Gebrauch des Streudiagramms in der Spektral analyse. In: R. Ritscht — G. Holdt: Emissionsspektroskopie. Akademia — Verlag (Berlin) 411 pp.

HADDON, M. J. — PANTHONY, D. A., 1980: Specific extraction method for the determination of gold in ores and products. Analyst (London), 105, pp. 371—378.

KHITROV, V. G. — BELOUSOV, G. E. — SYCHKOVA, V. A., 1980: Metodika spektrochimičeskovo analiza prirodnych i promyšlennych materialov na platinovyje metally. Ž. prikl. spektroskopiji (Minsk) 5, pp. 773—776.

KHITROV, V. G. — KORTMAN, R. V., 1974: Rezuľtaty mežlaboratornoj ocenki kačestva opredelenij mikroelementov v gornych porodach. Obzor, Serija — Laboratornyje i technologičeskije issledovanija i obogaščenije mineraľnogo syrja. (Moscow) 48 pp.

KONTAS, E., 1981: Rapid determination of gold by flameless atomic spectrometry in the ppb and ppm ranges without organic solvent extraction. Atomic spectroscopy (Norwalk, Conn.), 2, 2, pp. 60—61.

MEDVEĎ, J. — MARTINY E. — PLŠKO, E., 1985: Spektrochemické stanovenie zlata v geologických materiáloch po nabohatení pomocou vymieňačov iónov. Hodnotenie postupov stanovenia rozptýlených prvkov. Záver. zpr. ŠPZV č. II-4-6/05. Manuscript, Geol. Institute SAV (Bratislava), pp. 75—86.

OWEN, D. B., 1966: Sbornik statističeskich tablic. Vyčisliteľnyj centr AN SSSR, Moscow, 586 pp.

PLŠKO, E., 1964: Sledovanie odparovania nevodivých materiálov z uhlíkových elektród pri spektrálnej analýze. Chem. zvesti (Bratislava), 19, pp. 544—550.

PLŠKO, E. — FLORIÁN, K., 1980: The comparison of the reliability of different procedures for the blackening transformation. VI-th Czechoslovak spectroscopic conference, September 1—5 Nitra, pp. 149—162.

RUBEŠKA, I. — KOREČKOVÁ, J. — WEISS, D., 1977: The determination of gold and palladium in geological materials by atomic absorption after extraction with dibutyl sulfide. AAN (Broockfield) 16, 1, pp. 1—3.

RUSANOV, A. K., 1960: Količestvennoje opredelenije redkich i rassejanych elementov. Gosgeoltechizdat, Moscow, 197 pp.

SIGHINOLFI, G. P. — SANTOS, A. M., 1976: Determination of gold in geological samples at parts per miliard levels by AA flameless spectrocsopy. Microchim. Acta, (Oxford), II. pp. 33—40.

SIGHINOLFI, G. P. — GORGONI, C., 1977: Gold distribution in the Ivrea — Verbono gabbroic complex. Chem. geol. (Amsterdam), 20, pp. 99—107.

SAVINOVA, E. M. — MALOFEYEVA, G. I. — DETISTOVA, A. L. — MARCHEVA, E. V., 1984: Sorbcionno-spektraľnyj metod opredelenija platinovych metallov i zolota v prirodnych objektach. Inst. geochimii i analitičeskoj chimii im. V. I. Vernadskovo AN SSSR (Moscow), Manuscript.

SHCHERBAKOV, J. G. — PEREZHOGIN, G. A., 1964: K geochimii zolota. Geokhimya (Moscow), pp. 518—528.

STREŠKO, V., 1979: Stanovenie zlata v kremičitanových horninách atómovou absorpčnou spektrometriou. Symposium on petrogenesis and geochemistry of geological processes. Bratislava, Veda, vyd. SAV, pp. 291—297.

TARASOVA, I. I. — DUDENKOVA, L. S. — KHITROV, V. G., 1974: O chimikospektraľnom opredeleniji metallov platinovoj gruppy i zolota v produktach pererabotky mednonikelevych rud. Ž. anal. chim. (Moscow), 29, 11, pp. 2147—2149.

VINOGRADOV, A. P., 1962: Sredneje soderžanije chimičeskich elementov v glavnych tipach izverženných gornych porod zemnoj kory. Geokhimya (Moscow), 7, pp. 555—571.

VINCENT, E. A. – CROCKET, J. H., 1960: Studies in the geochemistry of gold, I. The distribution of gold in rocks and minerals of the Skaergaard Intrusion, east Greenland. Geochim. Cosmochim. Acta (Oxford), 13, pp. 130—142.

VOROBYEVA, G. A. – ZOLOTOV, J. A. – IZOSENKOVA, L. A. – KARYAKIN, A. V. – PAVLENKO, L. I. – PETRUCHIN, O. M. – SERYAKOVA, I. U. – SIMENOVA, L. V. – SHEVCHENKO, V. N., 1974: Ekstrakcionnoje koncentrirovanije platinovych metalov i zolota difeniltiomočevinoj s posledujuščim spektraľnym opredeleniem. Ž. anal. chim. (Moscow), 29, pp. 497—503.

WEISS, D. – BOUBERLOVÁ, L. – RUBEŠKA, I., 1975: Prospekční stanovení zlata v nerostných surovinách. Výskumní spr., ÚÚG, Praha, pp. 85—95.

WEISS, D. et al., 1983: Metody chemické analýzy nerostných surovin. ÚÚG, Praha, pp. 103—106.

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