PRECONCENTRATION AND SEPARATION OF GOLD ON MODIFIED SILICA GEL

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Selective preconcentration of gold in the form of ion associates of Au(III) chloro complex or Au(I) cyano complex with quaternary bases was studied using modified silica gel. Solutions containing gold in the presence of the complexing anion and a quaternary base were pumped through a Separon™ SGX C18 column. After elution with 96 vol.% ethanol, the eluate was evaporated in the presence a complexing agent (chloride or cyanide). The resulting aqueous solutions were analyzed with inductively coupled plasma atomic emission spectrometry. The influence of concentration of onium salts, chlorides, nitrates, and the influence of the sample volume on the sorption were studied. The sorption flow rate and the elution volume were optimized, and the separation from a geological sample matrix was verified. The best recovery (100%) of preconcentration of Au(III) chloro complex was obtained with [1-(ethoxycarbonyl)pentadecyl]trimethylammonium bromide and 1-hexadecylpyridinium chloride at concentrations of 0.006 and 0.004 mol dm^{-3}, respectively. The sorption flow rate of a sample may vary in the range 0.4–7 cm^3 min^{-1}, the elution volume was between 5 and 6 cm^3. The recovery decreased with increasing sample volume above 250 cm^3 and was diminished by 10% in the presence of nitrates above 0.4 mol dm^{-3}. Major accompanying elements Fe and Mn, which considerably interfere at the Au I 242.795 nm line, were quantitatively separated from gold. A Czech certified reference material 1001 Mokrsko was analyzed using the developed preconcentration technique and inductively coupled plasma atomic emission spectrometry, inductively coupled plasma mass spectrometry, and atomic absorption spectrometry. Sorption of ion associates of Au(I) cyano complex was also efficient.

Key words: Ion associates; Quaternary ammonium salts; Silica gel C18; Gold; Sorbents; Inductively coupled plasma atomic emission spectrometry.

Gold shows very low natural concentrations on the Earth. The average concentration in earth crust (clark value) was reported[1] to be 4 ng Au per g, the concentration of 0.05 ng cm^{-3} of Au was determined in sea water, and values of 0.086 and 0.2 ng cm^{-3} were found in river water and spring water, respectively[2]. The minimum concentration of Au of 2 g t^{-1} in ore is required for the profitable mining.

Preconcentration and separation techniques are necessary for reliable determination of traces of gold due to its low concentrations. In the analysis by molecular absorption spectrophotometry, extraction of ionic associates of complex anions $[AuCl_4]^-$, $[AuBr_4]^-$ with basic components (rhodamine B, trioctylphosphine oxide) was employed. Extraction fluorimetry of the Au(III) complex with 5-(4-dimethylaminobenzyliden)rhodanine in chloroform was used for the determination of gold in silicates and sulfidic ores. The stripping voltammetry was employed after extraction of the ionic associate with methyltrioctylammonium chloride. Coprecipitation of gold with Hg, Te or Se as collectors was applied to preconcentration[2]. The neutron activation analysis followed after extraction or dokimastic preconcentration, yields the detection limit of $5 \cdot 10^{-4}$ μg Au (refs[2,3]).

Ionic associates or chelates containing Au(III) or Au(I) were extracted from HCl into organic solvents and efficient extractions with *N*,*N*-diethyldithiocarbamate, thiooxine, dithizone, *etc.* were described[3]. Gold in the form of $[AuCl_4]^-$ was extracted from 4 M HCl with trioctylamine into kerosene containing 20% of octan-1-ol[4]. Nondesulfurized fraction of crude oil distillate containing 0.2% of S and 19% of aromatic hydrocarbons was employed for the extraction of gold. The procedure was followed by the determination using flame atomic absorption spectrometry (FAAS) with limits of detection 0.03 and 0.001 mg dm^{-3} in organic and aqueous phases, respectively[5]. This method exhibited good agreement with results of commonly employed extraction with dibutyl sulfide (DBS). At present, atomic absorption spectrometry with electrothermal atomization (ETAAS) after extraction preconcentration is widely employed due to lower limits of detection[6,7].

Adsorption methods are now widely used as the most efficient procedures for separation and preconcentration of noble metals. Direct adsorption of solvent-extracted gold on a highly selective (Au, platinum group metals, Hg) chelating anion exchange resin Srafion NMRR was followed by the neutron activation analysis for the determination of gold in meteorites[8]. Preconcentration of gold on chelating resin Spheron–Thiol, subsequent decomposition and emission spectrography was applied to the analysis of geological samples with the limit of detection 0.5 μg kg^{-1} of Au (ref.[9]). Various new chelating resins were synthesized and applied to preconcentration and separation of Au and selected platinum group metals[10–13].

For the separation of ionic associates of bromo complexes of Pt(II), Pt(IV), Pd(II), and Au(III) with onium cations (tetramethylammonium, tetrabutylammonium, hexadecyltrimethylamonium), the reverse-phase highperformance liquid chromatography on a modified silica gel C18 was used[14].

Recently, modified silica gel Separon SGX C18 was found to be suitable for the preconcentration of 2–20 μg of Pt from 0.1 M HCl in the presence of cationic surfactants, in particular benzyl(dodecyl)dimethylammonium bromide, with subsequent elution with 96 vol.% ethanol. The recovery was 86–110% for 2 μg of Pt. The final emission spectrometry of Pt in a plant ash matrix was carried out in 15 A dc arc[15,16]. The preconcentration of ion pairs is also efficient for some other elements, such as thallium (0.02–20 μg), which was preconcentrated on silica gel C18 from 0.1 M HCl in the presence of various cationic surfactants as ion pairs with tetrachlorothallate(III) and subsequently eluted with 96 vol.% ethanol. Atomic emission spectrometry in N_2O-acetylene flame was suitable for the analysis of plants[17], water or aqueous extracts of wastes and soils[18]. A simple selective preconcentration of Pt and Pd in the form of ion pairs of Pt(IV) and Pd(II) chloro complexes with cationic surfactant Septonex® on Separon™ SGX C18 column was used in combination with inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) for the determination of these elements in airborne particulate material and the engine soot NIES No. 8. In addition to Pt and Pd sorption, that of Au, Ru, Rh, Os, and Ir was studied[19].

The aim of the present work was to investigate the possibilities of the selective preconcentration of gold in the form of ion pairs of chloro complexes of Au(III) and cyano complexes of Au(I) with cationic surfactants on modified silica gel C18 followed by the determination with ICP-AES. The method was used for the determination of gold in a certified reference material of gold ore and in the waste rock.

EXPERIMENTAL

Instruments and Operating Conditions

An ICP atomic emission spectrometer JY-170 Ultrace (Jobin–Yvon, France) with laterally viewed plasma was operated at the standard power input 1 kW of a 40.68 MHz generator. The outer, sheath and nebulizer gas flow rates were 14.0, 0.2, and 0.75 $dm^3\ min^{-1}$ of Ar, respectively. A standard Meinhard nebulizer with a cyclonic spray chamber was operated at the pressure 300 kPa and the sample uptake rate 1 $cm^3\ min^{-1}$ controlled using a Gilson peristaltic pump. The standard observation height 10 mm above the load coil was employed. Optimum operating conditions of the plasma source were verified by measuring the signal-to-background ratio of the Au I 242.795 nm line. The JY-170 instrument is provided with a Czerny–Turner monochromator and a Paschen–Runge polychromator. The 1-m monochromator is equipped with two gratings; one for the wavelength range 160–430 nm

(4 320 mm^{-1}), the other for the range 160–780 nm (2 400 mm^{-1}). Throughout this work, the monochromator was used with the grating 4 320 mm^{-1} and a combination of entrance and exit slits 22 μm/15 μm. The instrument was controlled by means of the JYESS 4.05 software. The Gaussian measuring mode was mostly employed and the integration time was 0.5 s. Background correction points were selected at the wavelengths 242.7816 and 242.8122 nm based on scans acquired with potentially interfering accompanying elements Fe and Mn.

Analyses of real samples were checked by measuring with other techniques. An ICP-MS instrument Elan 6000 (Perkin–Elmer Sciex), installed at the Mendel University in Brno, Czech Republic, was operated at the power input 1 kW of the 40.68 MHz generator. The outer, intermediate and carrier gas flow rates were 17.0, 1.2, and 0.93 dm^3 min^{-1}, respectively. Sample solutions were pumped to a cross-flow nebulizer at the uptake rate of 1 cm^3 min^{-1}. The signal of gold was measured at m/z = 196.967.

An AAS instrument PE 3030 with a graphite furnace HGA 400 (Perkin–Elmer, Germany) of the Department of Analytical Chemistry of the Masaryk University in Brno was used for comparative measurements of geological samples. The Au 267.595 nm line was measured at the spectral bandwidth 0.7 nm with a background correction using a deuterium lamp. As a modifier, $Ni(NO_3)_2$ was used.

The sorption apparatus used consisted of a two-head multichannel peristaltic pump ID-100 (Skala Medical Technology Brno, Czech Republic) with adjustable speed, provided with peristaltic tubings of various diameters. Solutions were pumped through SilicaCart™ (Tessek Ltd., Prague, Czech Republic) cartridges 9 × 20 mm containing modified silica gel Separon™ SGX (particle diameter 60 μm).

Chemicals and Solutions

A standard stock solution containing 999 mg dm^{-3} Au in 1 M HCl was prepared by dissolution of a gold wire (Safina Co., Jesenice, Czech Republic) in the aqua regia. Working solutions were prepared by diluting the stock solution with 0.1 M HCl. Another standard stock solution of 1 000 mg dm^{-3} Au was prepared by dissolution of a gold powder (Safina Co.) in a solution of 0.12 M KCN. Working solutions were prepared from this cyanide stock solution by diluting with distilled water. Single-element standard stock solutions containing 1 000 mg dm^{-3} Mn, 1 000 mg dm^{-3} Fe, and 1 000 mg dm^{-3} Pt (Astasol®, Analytika Ltd., Prague, Czech Republic) were used for preparation of solutions for interference studies. 0.1 M aqueous stock solutions of the following cationic surfactants were prepared: [1-(ethoxycarbonyl)pentadecyl]trimethylammonium bromide (Septonex®); benzyldodecyldimethylammonium bromide (Ajatin®, both from Slovakofarma Co., Hlohovec, Slovak Republic); 1-hexadecylpyridinium chloride (CPC, Sigma Chemicals Co.); hexadecyl(trimethyl)ammonium bromide (CTAB), tetraphenylarsonium chloride (TPAC, both from Lachema Inc., Brno, Czech Republic). For elution, 96 vol.% ethanol, denaturated with 5 vol.% methanol, was ultrasonically deaerated. Other used chemicals were: HNO_3 (Merck, Darmstadt, Germany), HCl (Onex Ltd., Rožnov pod Radhoštěm, Czech Republic) KCl, KBr, KI, KCN, KSCN, KNO_3, $Mg(NO_3)_2 \cdot 6H_2O$, $FeNH_4(SO_4)_2 \cdot 12H_2O$ (all from Lachema Inc., Brno). All the chemicals were of analytical grade quality.

Sorption and Elution Procedures

The SilicaCart™ cartridge with sorbent was initially washed with 10 cm^3 of 96 vol.% ethanol, 5 cm^3 of distilled water and 10 cm^3 of aqueous solution of the quaternary salt in the same concentration used in sorbed samples. Solutions containing analyte in the presence of a proper anion and a quaternary base were then pumped through the cartridge. After sorption, the cartridge was washed with 5 cm^3 of water. As it was found, no desorption of sorbed ionic associate occurred by the action of distilled water. For desorption of ion associates of anionic complexes of gold with quaternary bases, 96 vol.% ethanol was pumped through the cartridge and an experimentally estimated volume of the eluate was collected in a calibrated test tube with 2.5 cm^3 of the solution containing complexing anion[15–19]. Then the ethanol was evaporated in a Teflon® dish under an infrared lamp, the residue was transferred into a volumetric flask (10 cm^3) and filled up to the mark. The sorption and desorption flow rates were 0.8 and 1.3 $cm^3\ min^{-1}$ if not otherwise stated. The evaporation of ethanol was performed to obviate the introduction of volatile solvent into the ICP discharge.

RESULTS AND DISCUSSION

Influence of Quaternary Onium Salts on ICP Emission Intensity of Au I 242.795 nm Line

The presence of significant concentration of an organic matrix in solution may bring an excessive plasma load. Therefore, the studied quaternary onium salts may affect both the excitation conditions and the efficiency of aerosol formation due to their surface-active effect[20]. On average, a 10%-depression of the Au net line intensity was observed in the presence of Septonex®, CPC, Ajatin®, CTAB, and TPAC in the concentration range from 10^{-3} to 10^{-2} mol dm^{-3}. These non-spectral interferences were constant within that range expected for use in a preconcentration procedure. The same effects were observed for several ICP instrumentations[21]. Consequently, the matrix was kept at appropriate concentration also in calibration samples and other comparative solutions.

Preconcentration and Separation of Gold by Sorption of Ion Associate of Au(III) Chloro Complex with Onium Cations on Modified Silica Gel C18

Elution Volumes, Recovery of Preconcentration and Reproducibility

The amount of ethanol necessary for elution of ion associates was studied for Septonex®, CPC, Ajatin®, CTAB, and TPAC. An amount of 50 cm^3 of solution containing 20 μg of Au in the presence of 0.006 M onium salt and 0.1 M HCl was brought onto the column. The elution was performed in 1-cm^3 fractions. This implies, from the elution profiles in Table I, that quantitative desorption of ion associates of the chloro complex of Au(III) with Septonex® or CTAB occurred within 5 cm^3. For the elution of the associates with CPC or Ajatin®, the volumes of 6 and 7 cm^3 of ethanol were necessary, respectively. However, the real elution volume was lower because of approximately 0.8 cm^3 dead volume of the peristaltic tubing and capillaries. Desorption of TPAC ion associate was not quantitative even when employing 10 cm^3 of ethanol, which will be discussed later.

For each quaternary salt, a set of test samples containing 20 μg of Au in 50 cm^3 of solution in the presence of 0.1 M HCl was prepared at the concentrations of the onium salts from 10^{-4} to 10^{-2} mol dm^{-3}. The recovery determination was based on the amount of analyte brought onto the column and the amount of analyte eluted with ethanol. The preconcentration was repeated at each concentration ten times for all quaternary bases, and the average confidence intervals were found to be ±3 rel.%.

Quantitative sorption was already achieved at 0.002 M CPC (curve *1* in Fig. 1). Almost the same dependence was obtained for Septonex®. Less sta-

TABLE I

Elution with ethanol of ion associates of $[AuCl_4]^-$ with quaternary onium cations sorbed on modified silica gel Separon™ SGX C18 with ethanol. Limit of detection[25,26] x_D = 0.02 μg Au ($3\sigma_{BL}$)

Ethanol volume, cm^3	Au (μg) found using quaternary onium salts				
	Septonex®	CTAB	CPC	Ajatin®	TPAC
1	16.73	16.64	14.45	16.15	5.71
2	3.10	2.74	4.08	2.96	1.43
3	0.19	0.48	0.88	0.17	0.37
4	0.05	0.14	0.38	0.08	0.29
5	0.02	0.05	0.15	0.08	0.48
6	<0.02	<0.02	0.12	0.07	0.18
7	<0.02	<0.02	<0.02	0.05	0.21
8	<0.02	<0.02	<0.02	<0.02	0.24
9	<0.02	<0.02	<0.02	<0.02	0.80
10	<0.02	<0.02	<0.02	<0.02	0.22
Total Au, μg	20.09	20.05	20.06	19.56	9.93

ble ionic associates were obtained with CTAB (curve *2*, Fig. 1) and Ajatin® when the quantitative recovery was reached at higher concentration, 0.008 mol dm^{-3}. However, this concentration caused foaming of solutions and blocking of columns. Tetraphenylarsonium chloride yielded almost quantitative recovery at 0.004 mol dm^{-3} (curve *3*, Fig. 1) but a considerable decrease followed when increasing the concentration. This quaternary base was frequently used in the past for precipitation of anions like ReO_4^-, MnO_4^-, TcO_4^-, IO_4^-, and, *e.g.*, for extraction of $[AuCl_4]^-$ with 0.05 M TPAC in chloroform[3]. Therefore, it could be expected that some precipitation occurred in the column and elution with ethanol was hindered. Consequently, Septonex® and CPC were employed for further experiments at concentrations 0.006 and 0.004 mol dm^{-3}, respectively. No column blocking was observed at these concentrations.

Sorption from solutions that contained only Au(III) in 0.1 M HCl without addition of a quaternary base was also tested. First, the column was washed with 10 cm^3 of ethanol, 5 cm^3 of distilled water and then with 10 cm^3 of 0.006 M Septonex® or 0.004 M CPCA to fix quaternary groups on the sorbent. Then 50 cm^3 of a solution containing 20 μg of Au(III) in 0.1 M HCl was pumped through the column. Elution was accomplished using 6 cm^3 of ethanol. The recovery occurred in confidence intervals (73 ± 5)% for Septonex® and (76 ± 2)% for CPC. Therefore, an excess of a quaternary base in sorbed solution is necessary for quantitative recovery.

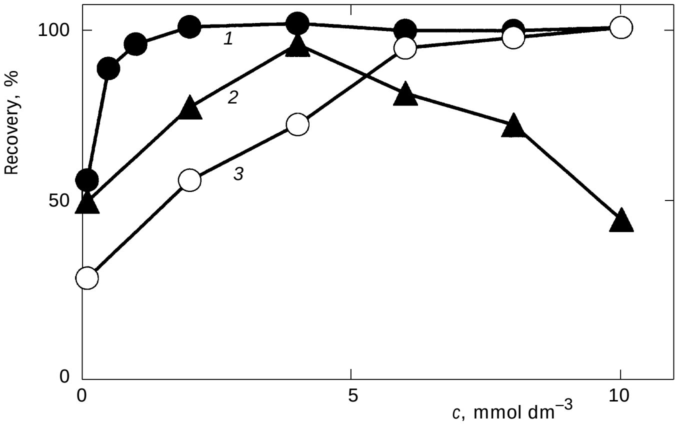

FIG. 1

Influence of concentration of CPC (*1*), CTAB (*2*), and TPAC (*3*) on recovery of 20 μg of Au in 50 cm^3 of solution in the presence of 0.006 M onium salt and 0.1 M HCl, elution with ethanol

Reproducibility of the sorption/elution procedure was found to be 2% RSD both for Septonex® and CPC. The solutions containing 20 μg of Au(III) in 50 cm^3, prepared in 0.1 M HCl with 0.006 M Septonex® or 0.004 M CPC, were pumped through the column at a flow rate of 0.8 $cm^3\ min^{-1}$. The sorbed associate was then eluted with ethanol at a flow rate of 1.3 $cm^3\ min^{-1}$. The procedure was repeated ten times and estimates of the recovery were (101 ± 2) and (100 ± 2)% for Septonex® and CPC, respectively.

Influence of Sorption Flow Rate on Recovery

The sorption was studied using solutions containing 20 μg of Au(III) in 50 cm^3, prepared in 0.1 M HCl with 0.006 M Septonex® or 0.004 M CPC, at flow rates between 0.4 and 8.5 $cm^3\ min^{-1}$. The recovery, practically independent of the flow rate between 0.4 and 7 $cm^3\ min^{-1}$, was in the range from (97 ± 4) to (101 ± 3)% for both onium salts, the ± denoting a confidence interval. At 8 $cm^3\ min^{-1}$ the recovery dropped to (95 ± 5)% and a significant decrease commenced. Consequently, a considerably high pumping rate can be employed for the preconcentration procedure.

Influence of Concentration of Chlorides, Nitrates and Acids on Recovery

The recovery for solutions containing 20 μg of Au(III) in 50 cm^3 at a concentration of 0.006 M Septonex® or 0.004 M CPC was independent on the concentration of chlorides in the range from 0.01 to 0.5 M KCl. Hydrochloric acid had no influence on the recovery up to 0.4 M concentration but a significant decrease occurred for higher concentrations in the case of Septonex® (curve *1*, Fig. 2) or CPC. This might be due to possible degradation of sorbent by the action of hydrochloric acid. As ore samples and other geological materials subjected to the determination of gold are usually treated with aqua regia, the influence of nitrates and nitric acid on the recovery was studied. The efficiency of sorption of the Septonex® associate decreased in the presence of 0.1 M nitrate to 90% and was constant up to 0.4 M KNO_3 (curve *2*, Fig. 2). The nitrate probably participates in the competitive formation of ion associate with a quaternary base. Moreover, in the case of CPC, precipitation of the ion associate occurred at KNO_3 concentrations above 0.3 mol dm^{-3} and made the sorption impossible. Nitric acid above 0.1 M concentrations also diminished the efficiency of sorption of the Septonex® associate because of competition of the nitrate anion and, probably, the degradation of sorbent could occur at higher acid concentrations (curve *3*, Fig. 2).

Influence of Sample Volume and Au(III) Concentration on Recovery

Recovery was studied for solution volumes in the range from 50 to 1 000 cm^3. Each solution contained 20 μg of Au(III) in 0.1 M HCl with 0.006 M Septonex® or 0.004 M CPC. The sorption flow rate was 0.8 cm^3 min^{-1}. It implies from dependences in Fig. 3 that the quantitative sorption is possible with sample volumes smaller than 250 cm^3. The same results were obtained at the flow rate 4 cm^3 min^{-1}. A possible reason for the sorption decrease might be washing-out of the sorbed associate with a large volume of solution containing a quaternary base.

Sorption of gold from a series of 100 cm^3 solutions containing 5–200 ng cm^{-3} of Au(III) in the presence of 0.006 M Septonex® or 0.004 M PC and 0.1 M HCl revealed that quantitative sorption occurred in the range from 200 to 20 ng cm^{-3} of Au. For the concentrations lower than 20 ng cm^{-3}, the recovery was still higher than 90%.

Spectral Interferences and Separation of Gold from Model Matrix

The analytical line Au I 242.795 nm was used for all experiments as the most sensitive and with minimum spectral interferences. However, in the

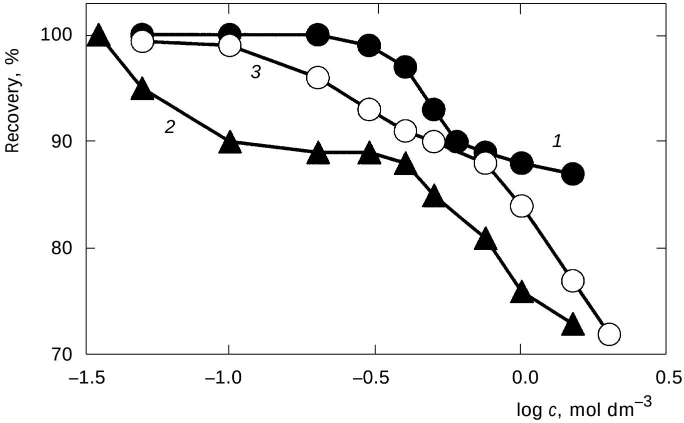

FIG. 2

Influence of concentration of HCl (*1*), KNO_3 (*2*), and HNO_3 (*3*) on recovery of 20 μg of Au in 50 cm^3 of solution in the presence of 0.006 M Septonex®

analysis of geological samples spectral interferences at this line can be expected from W, Mn, Pt, Sr, Mo, and Fe (refs[22,23]). The most serious spectral overlap is caused by the unresolved line of manganese, Mn 242.793 nm (Fig. 4). In the presence of excess of iron, the unspecified parallel background shift combined with the sloping background caused by the vicinity of the Fe 242.805 nm line occur (Fig. 4). Weak lines of other possible ac-

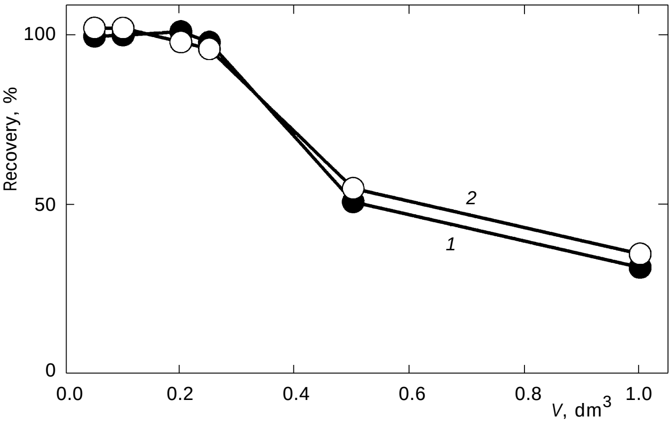

Fig. 3

Influence of the sample volume brought onto the column on recovery of 20 μg of Au in the presence of 0.006 M Septonex® (*1*) or 0.004 M CPC (*2*) in 0.1 M HCl

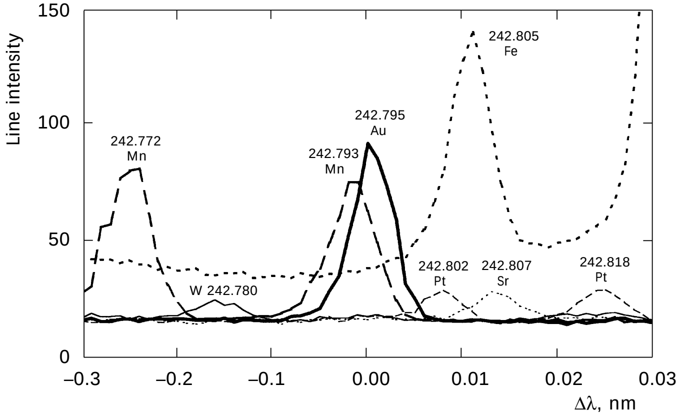

Fig. 4

Spectral scans in the vicinity of Au I 242.796 nm line recorded for gold (0.2 mg dm^{-3}) and possible accompanying elements (mg dm^{-3}): Mn 10, W 10.1, Sr 10, Pt 9.8, and Fe 1 000 companying elements are well resolved, as follows from Fig. 4, where the spectra of 0.2 mg dm^{-3} Au, 10 mg dm^{-3} Mn, 10.1 mg dm^{-3} W, 10 mg dm^{-3} Sr, 9.8 mg dm^{-3} Pt, and 1 000 mg dm^{-3} Fe are recorded. Iron and manganese are major constituents of geological samples and, therefore, removal of these elements from analyzed samples is the analytical step of vital importance for preserving the selectivity and the limit of detection.

Separation of iron and manganese from gold was studied with 100-cm^3 solutions containing 20 µg dm^{-3} Au, 1 000 mg dm^{-3} Fe, and 10 mg dm^{-3} Mn in the presence of 0.006 M Septonex® or 0.004 M CPC and 0.1 M HCl. Iron and manganes were added as chlorides. Ethanolic eluates were evaporated and the resulting aqueous solutions were filled up to 10 cm^3. Consequently, the preconcentration factor was 10. Concentration of Fe and Mn in eluates was determined using the lines Fe II 238.204 nm and Mn II 257.610 nm. It follows from the results presented in Table II that iron and manganese were completely separated from gold, which was quantitatively preconcentrated. The efficiencies of sorption of iron and manganese were only about 0.001 and 0.004%, respectively. In spite of the existence in solutions of $[FeCl_4]^-$, which could possibly form ion associates with quaternary salts, no sorption of Fe occurred.

Calibration and Limit of Detection

A four-point calibration curve was used in the concentration range 0–3.4 mg dm^{-3} Au, with the correlation coefficient 0.99995 and the relative uncertainty on centroid ±5.3% calculated from published relations[24]. Calibration solutions were prepared in 0.1 M HCl with 0.006 M Septonex®. Very

TABLE II
Separation of gold (0.020 mg dm^{-3}) from excess of Fe (1 000 mg dm^{-3}) and Mn (10 mg dm^{-3}) in 100 cm^3 of a solution

Quaternary salt	Recovery[a], mg dm^{-3}		
	Au	Fe	Mn
Septonex®	0.193 ± 0.018	0.118 ± 0.095	0.0044 ± 0.0026
CPC	0.215 ± 0.016	0.075 ± 0.046	0.0043 ± 0.0012

[a] Values describe the composition of 10-cm^3 analyzed solution prepared from eluate. Preconcentration factor is 10.

similar results were obtained for CPC. The limit of detection in 0.006 M Septonex® based on 3σ definition[25,26] was 2 ng cm^{-3}. This value is in good agreement with the values obtained using other ICP emission spectrometers at lateral or axial viewing (ng cm^{-3}): 9 and 3 for Perkin–Elmer Optima 3000 DV, lateral and axial, respectively; 3 for Jobin–Yvon JY-138 axial; 4 for Jobin–Yvon JY-166 axial; 7 for Thermo Jarrel–Ash IRIS axial[21].

Preconcentration and Separation of Gold by Sorbing Ion Associate of Au(I) Cyano Complex with Onium Cations on Modified Silica Gel C18

The cyanide method of gold extraction from ores was used for the first time by Mac Arthur and Forrest in 1886. The formation of $[Au(CN)_2]^-$ was assumed to occur also when dissolving the gold powder in an excess of KCN. This stable cyano complex $[Au(CN)_2]^-$ could be possibly employed for preconcentration of gold as ion associate. The stability constant of $[AuCl_4]^-$, defined as $[ML_4]/([M(OH)_4][H]^4[L]^4)$, is equal to log β_4 = 29.6, while the stability constant of $[Au(CN)_2]^-$ is reported to be log β_2 = 38.3 (ref.[27]). The higher stability of the cyano complex might prevent it from hydrolysis and thus ensure higher efficiency of sorption.

The influence of concentration of onium salts on recovery was studied for Septonex®, CPC, Ajatin®, CTAB, and TPAC in the concentration range 10^{-3}–10^{-2} mol dm^{-3}. The test samples contained 20 μg of Au in 50 cm^3 of solution in the presence of 0.0005 M KCN and a given concentration of the onium salt. The sorption and elution procedures were the same as for the Au(III) chloro complex with the exception that the eluates were filled up with distilled water. For all the employed quaternary bases, the recovery of preconcentration was equal to (99.5 ± 4.4)% over the studied concentration range. Consequently, the recovery was considerably improved for Ajatin®, CTAB, and TPAC in comparison with sorption of the ion associate of Au(III) chloro complex. The dependence of sorption efficiency with increasing concentration of KNO_3 was identical with that observed in sorption of the associate with $[AuCl_4]^-$. Similarly, the decrease in sorption efficiency with increasing sample volume showed the same course as in the case of $[AuCl_4]^-$.

It can be concluded that the presence of CN^- improves the efficiency of sorption at lower concentrations of quaternary salts in comparison to $[AuCl_4]^-$. However, the competitive sorption of associate with NO_3^- as well as the wash-out of the sorbed Au associate with a large volume of the sample solution containing onium salt remain to be common limitations.

Determination of Gold in Geological Samples

The Czech certified reference material (CRM) 1001, the auriferous ore "Mokrsko", was analyzed using the method based on preconcentration and separation of $[AuCl_4]^-$ as ion associates with Septonex® and CPC on modified silica gel Separon™ SGX C18. The composition of this CRM is given in Table III.

A sample (10 g) was left standing overnight with aqua regia, then digested on a hotplate under reflux condenser for 2 h and the leachate was evaporated to syrupy consistence. After diluting with 0.1 M HCl and filtration, the stock solution of Septonex® was added and the sample was filled up to 100 cm^3 with 0.1 M HCl. After sorption on a column (flow rate 0.8 cm^3 min^{-1}), desorption with 5 cm^3 of 96 vol.% ethanol was performed and the eluate was evaporated with 5 cm^3 of 0.1 M HCl under the infrared lamp. The residual solution (*ca* 4–5 cm^3) was transferred into a volumetric flask (10 cm^3) and filled up to the mark with 0.1 M HCl. The decomposition was repeated three times.

Samples were analyzed with ICP-AES using a calibration curve and the standard addition method. The standard addition determination was re-

TABLE III
Certified values of Czech certified reference material No. 1001 (auriferous ore Mokrsko)[a]

Constituent	%	Constituent	mg kg^{-1}
SiO_2	66.15 ± 0.27	As	876.5 ± 75.5
TiO_2	0.39 ± 0.02	Au	2.5 ± 0.2
Al_2O_3	14.06 ± 0.27	Cr	47.7 ± 4.5
Fe_2O_3[b]	5.55 ± 0.09	Cu	35.9 ± 2.8
MgO	1.81 ± 0.04	Ga	12.9 ± 1.4
CaO	4.09 ± 0.10	Sr	187.7 ± 18.3
BaO	0.066 ± 0.005	V	96.4 ± 14.3
MnO[b]	0.082 ± 0.004	Y	14.2 ± 2.4
Na_2O	3.08 ± 0.06	Zr	81.0 ± 9.2
K_2O	1.92 ± 0.07		

[a] Czech Geological Institute Prague. [b] Interfering constituents.

peated with different additions of Au(III) solution (see Table IV). Comparative analyses were performed with electrothermal AAS and ICP-MS using directly the aqua regia leachate after evaporation and dilution with 0.1 M HCl. Analyses with ICP-MS were carried out at the Institute of Chemistry and Biochemistry of the Mendel Agricultural University in Brno. Determination of gold using ETAAS after decomposition with aqua regia and extraction with DBS in toluene was performed independently in Geological Survey Ostrava, state company, establishment Brno, in the period of several years[28] (Table IV).

It follows from Table IV that at the level of significance $\alpha = 0.05$, there is no statistically significant difference between results obtained by sorption preconcentration and the certified value. The values obtained using ICP-MS and ETAAS after extraction with DBS/toluene demonstrate the possible scatter of results for different sampling of the reference material as well as the bias of various analytical techniques.

A sample "Sludge II" from the sulfide mud pit from the gold deposit Zlaté Hory (Czech Republic) was analyzed after preconcentration of ion associate of $[AuCl_4]^-$ with Septonex® and CPC. The residual gold in the sludge can be exploited by biohydrometalurgical leaching if the metal is bound in the lattice of pyrite or arsenopyrite[29]. After biodegradation of these sulfides, gold can be easily extracted with cyanide or thiourea. A profitable limit is above

TABLE IV
Determination of gold in the Czech certified reference material No. 1001 (Mokrsko)

Method	Medium	Evaluation	$w(Au)^a$, mg kg^{-1}
ICP-AES	Septonex®/HCl	Calibration curve	2.28 ± 0.40
ICP-AES	CPC/HCl	Calibration curve	2.29 ± 0.20
ICP-AES	Septonex®/HCl	Standard addition (1)	2.30 ± 0.20
ICP-AES	Septonex®/HCl	Standard addition (2)	2.29 ± 0.20
ICP-MS	Aqua regia/HCl	Calibration curve	2.10 ± 0.06
ETAAS	Aqua regia/HCl	Standard addition	2.28 ± 0.39
ETAAS	DBS/toluene	Calibration curve	2.67 ± 0.17
Certified value			2.5 ± 0.2

[a] Confidence intervals were calculated at the level of significance $\alpha = 0.05$ for number of repetitions $n = 3$.

2 g t^{-1} of Au. The composition of the Sludge II sample[30] is given in Table V. From the results of determination of gold in Sludge II presented in Table VI it is evident that the concentration of gold is below the required limit.

TABLE V
Composition of "Sludge II" from the Zlaté Hory mining

Constituent	%	Constituent	%
SiO_2	12.60	MnO[a]	0.08
TiO_2	traces	Fe_2O_3	2.34
Al_2O_3	1.66	FeO	38.66
CaO	0.64	Total Fe[a] (calculated)[b]	31.69
MgO	0.82	S	40.41
K_2O	0.29		
Na_2O	0.20		

[a] Interfering constituents. [b] Total % (m/m) of Fe calculated as a sum of Fe^{II} and Fe^{III}.

TABLE VI
Determination of gold in "Sludge II" from the mud pit of the Zlaté Hory mining

Method	Medium	Evaluation	w(Au), mg kg^{-1}
ICP-AES	Septonex®/HCl	Calibration curve	1.77 ± 0.23
ICP-AES	CPC/HCl	Calibration curve	1.80 ± 0.23
ICP-MS	Aqua regia/HCl	Calibration curve	1.25 ± 0.01
ETAAS	Aqua regia/HCl	Standard addition	1.48 ± 0.11

CONCLUSION

The sorption of ion associates of Au(III) chloro complexes with several quaternary salts on modified silica gel was studied with the aim of preconcentration of gold and its separation from geological matrix. The most efficient onium salts were found to be [1-(ethoxycarbonyl)pentadecyl]trimethylammonium bromide (Septonex®) and 1-hexadecylpyridinium chloride. The quantitative recovery was also found for ion associate of Au(I) cyano complexes with Septonex®, CPC, Ajatin®, CTAB, and TPAC. A method of separation and preconcentration of gold was developed which allows quantitative removal of the most significant spectral interferents of Au in ICP emission spectrometry, Fe and Mn. Iron is the most abundant element in sulfidic ores present in a leachable form. The Czech certified reference geological material No. 1001 (auriferic ore Mokrsko) as well as a sludge from the mud pit were successfully analyzed. Ion associates of cyanide complex of Au(I) with quaternary bases afford very good recovery, which is the aim of our further study.

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