Spectrophotometric determination of gold using Septonex

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The formation of the ion associate of the $[AuCl_4]^-$ complex anion with carbethoxypentadecyltrimethylammonium bromide (Septonex) was studied. A new spectrophotometric method for the determination of µg amounts of Au(III) per cm^{-3} using Septonex was developed on the basis of the determined optimal conditions ($\lambda = 332$ nm, pH $= 0.1$—1.0).

Было изучено образование ионного ассоциата комплексного аниона $[AuCl_4]^-$ с карбэтоксипентадецилтриметиламмонийбромидом (Septonex). Новый спектрофотометрический метод определения мкг Au(III) $см^{-3}$ с использованием указанного соединения был разработан с учетом оптимальных условий ($\lambda = 332$ нм, pH $= 0,1$—$1,0$).

In addition to the most common method, based on the formation of the complex with *p*-dimethylaminobenzylidene rhodanine, complex halide ions, $[AuCl_4]^-$ and $[AuBr_4]^-$, and the formation of ion associates of these anions with a number of reagents, *e.g.* with organic dyes (Rhodamine B, Methyl violet), amines, *etc.* [1] are frequently employed in the spectrophotometric determination of gold. The ion associates formed are generally poorly soluble in water and thus must be extracted into a suitable organic solvent.

The formation of the ion associate of the $[AuCl_4]^-$ complex anion with carbethoxypentadecyltrimethylammonium bromide was used in this work. The solubility of this associate in water permits a very simple and rapid determination of Au(III) ions.

Experimental

Instruments and reagents

Spectrophotometric measurements were carried out on a Unicam SP 800 instrument (Pye-Unicam, Cambridge) and on a Spekol instrument (Zeiss, Jena) using quartz cuvettes with an internal dimension of 2.00 cm. The solution acidity was measured with a PHM 52

pH-meter (Radiometer, Copenhagen) with a G 202 B glass electrode and a saturated calomel electrode.

The stock solution of 1×10^{-2} mol dm^{-3} trivalent gold was prepared by dissolving 0.19697 g of pure metal in several cm^3 of aqua regia. After dissolving, 0.2 g of NaCl was added and the solution was evaporated to dryness on a water bath. The residue was dissolved in the necessary amount of concentrated HCl and diluted to 100 cm^3 with 1 mol dm^{-3} HCl.

The 5×10^{-3} mol dm^{-3} Septonex solution (Slovakofarma, Czechoslovakia) was prepared by dissolving 0.5281 g of the substance in 250 cm^3 of distilled water.

The pH was adjusted using Walpole buffers [2] and 1 mol dm^{-3} HCl. In the study of the effect of the ionic strength, a 2 mol dm^{-3} KCl solution was used to adjust the ionic strength value. In the study of the character of the associate formed, the Ostion KS cation exchanger (Spolek pro chemickou a hutní výrobu, Czechoslovakia) and the Zerolit FF anion exchanger (Zerolit Ltd., England) were used.

Results and discussion

Study of absorption spectra

In 0.1—1 mol dm^{-3} HCl solutions the $[AuCl_4]^-$ complex anion yields an absorption maximum at a wavelength of 225 and also at 312 nm; the latter maximum was formerly used for the spectrophotometric determination of gold [3]. We have found that this maximum is shifted to a wavelength of 332 nm in the presence of Septonex, while the absorbance increases almost two-fold compared to the maximal absorbance of the $[AuCl_4]^-$ ion. The absorption spectra of $[AuCl_4]^-$, Septonex, and their reaction product are given in Fig. 1.

As Septonex is carbethoxypentadecyltrimethylammonium bromide, it was necessary to find whether the bathochromic and hyperchromic shifts of the absorption band of $[AuCl_4]^-$ in the presence of Septonex are not merely the results of the exchange reaction

$$[AuCl_4]^- + 4Br^- \rightleftharpoons [AuBr_4]^- + 4Cl^-$$
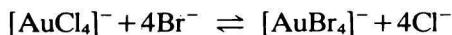
as it is well known that the $[AuBr_4]^-$ complex anion has an absorption band at 380 nm [4]. Consequently, the absorption spectra of a solution of $[AuCl_4]^-$ in the presence of Zephiramine cation active tenside, i.e. benzyldimethyltetradecylammonium chloride (as a concentration of 2×10^{-4} mol dm^{-3} Zephiramine produced turbidity in the solution, a concentration of 3×10^{-4} mol dm^{-3} was employed) and of potassium bromide were measured. The absorption curves obtained are depicted in Fig. 2. It is apparent from the figure that an exchange reaction does not occur under the described conditions because curve 1, corresponding to $[AuCl_4]^-$, and curve 2 for $[AuCl_4]^-$ in the presence of KBr are identical, while the curves for

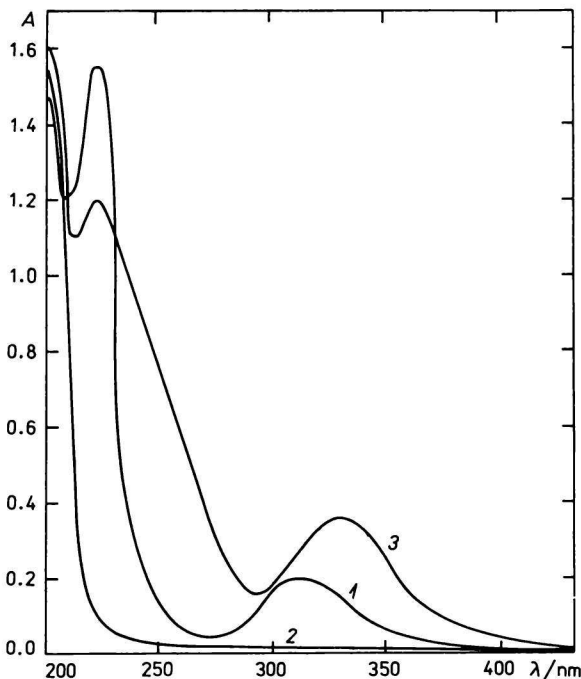Fig. 1. Absorption spectra of the ion associate and its components.
1. $[AuCl_4]^-$; 2. Septonex; 3. $[AuCl_4]^- +$ Septonex.
$c_{Au(III)} = 2 \times 10^{-5}$ mol dm^{-3}; $c_{Sept} = 2 \times 10^{-4}$ mol dm^{-3}; pH $= 0.7$.
Measurements carried out against water.

$[AuCl_4]^-$ in the presence of Septonex and Zephiramine (curves 3 and 4) exhibit bathochromic and hyperchromic shifts.

An increase in the concentration of Br$^-$ to a value of 2×10^{-3} mol dm^{-3} and a decrease in the acidity of the solution (pH 2.8) result in the formation of the $[AuBr_4]^-$ complex anion in solution with an absorbance maximum in the region of 370 nm, as is apparent from curves 5 and 6. This information must be employed in using this reaction for the spectrophotometric determination of Au(III) ions.

The extraction of the reaction product of $[AuCl_4]^-$ with Septonex and of both of these components from a polar solvent (water) into a solvent of a low polarity (chloroform) was studied to confirm the presence of the ion associate. While $[AuCl_4]^-$ is not extracted at all into chloroform and Septonex is extracted only partially, the extraction of their reaction product is practically quantitative. It can thus be assumed that the ion associate $[AuCl_4]^-$—Septonex of a low polarity is formed in the reaction.
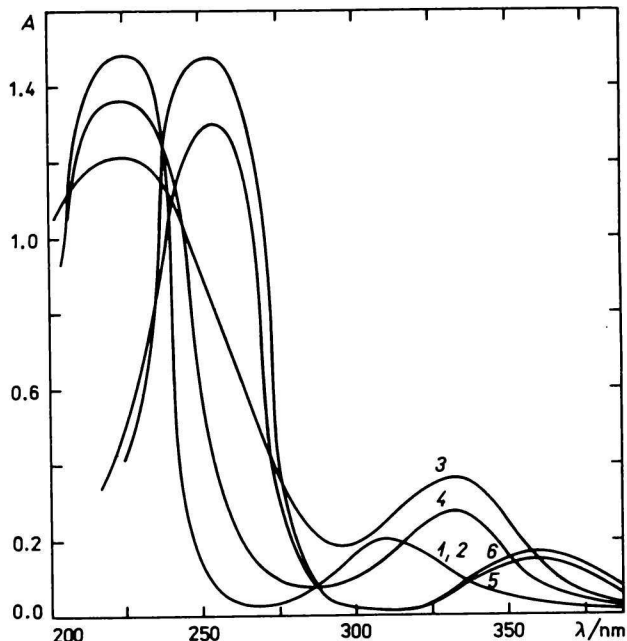
Fig. 2. Absorption spectra of $[AuCl_4]^-$ in the presence of Septonex, Zephiramine, and potassium bromide.

1. $[AuCl_4]^-$; *2.* $[AuCl_4]^- + KBr$; *3.* $[AuCl_4]^- + Septonex$; *4.* $[AuCl_4]^- + Zephiramine$.
$c_{Au(III)} = 2 \times 10^{-5}$ mol dm^{-3}; $c_{KBr} = 2 \times 10^{-4}$ mol dm^{-3}; $c_{Sept} = 2 \times 10^{-4}$ mol dm^{-3};
$c_{Zeph} = 3 \times 10^{-4}$ mol dm^{-3}; pH = 0.7.
5. $[AuCl_4]^- + Septonex$; *6.* $[AuCl_4]^- + KBr$.
$c_{Au(III)} = 2 \times 10^{-5}$ mol dm^{-3}; $c_{Sept} = 2 \times 10^{-3}$ mol dm^{-3}; $c_{KBr} = 2 \times 10^{-3}$ mol dm^{-3}; pH = 2.8.
Measurements carried out against a blank.

The ionic nature of the bond was demonstrated using an ion exchanger. A solution containing 3×10^{-5} mol dm^{-3} $[AuCl_4]^-$ and 3×10^{-4} mol dm^{-3} Septonex which had passed through the catex in the H^+ cycle yielded an absorption spectrum identical with that of $[AuCl_4]^-$ alone; thus the Septonex cation was retained on the ion exchanger. Similarly, a solution with the same composition which had passed through an anex in the OH^- cycle yielded an absorption spectrum identical with that of Septonex; the $[AuCl_4]^-$ anion was retained on the ion exchanger. This behaviour confirms the ionic nature of the bond.

Optimal reaction conditions, calibration curve

A constant absorbance value at 332 nm was attained in the pH interval from 0 to 1.0, the most suitable Septonex concentration is between 1.2×10^{-4} and $5 \times$

10^{-4} mol dm^{-3} at a gold concentration of 2×10^{-5} mol dm^{-3}; at lower Septonex concentrations a turbidity is formed in the solution. This fact is apparently connected with micelle formation in the solution, as the critical Septonex concentration at ionic strengths of 0.1 to 1.0 (adjusted using NaCl) is about 1.0×10^{-4} mol dm^{-3} [5].

The ion associate is formed immediately after mixing the components and the solution absorbance is then constant for 1 h, after which it slowly decreases.

The ionic strength value in the range 0.1—0.5 does not affect the absorbance; at higher ionic strength values the absorbance slowly decreases.

Under the determined optimal conditions ($\lambda = 332$ nm, pH $= 0.7$, $c_{Sept} = 2 \times 10^{-4}$ mol dm^{-3}) the Lambert—Beer law is obeyed in the range 2.4—10.2 µg Au(III) cm^{-3}. The calibration curve, obtained from six parallel measurements was evaluated by the linear regression method; the results are given in Table 1. The molar absorption coefficient was $\varepsilon_{332} = 1.8 \times 10^4$ dm^3 mol^{-1} cm^{-1} and the Sandell sensitivity [1] was $s = 5.8 \times 10^{-3}$ µg cm^{-2}.

Table 1

Statistical evaluation of calibration curves by the linear regression method

s	$v/\%$	b	a	$s_{x,y}$	s_a	s_b
0.0079—0.0157	1.8—7.9	0.1927	−0.0588	0.0056	0.0065	0.0022

s — standard deviation (obtained from the range [6]), v — variation coefficient [6], b — slope of the regression straight line, a — shift of the regression straight line, $s_{x,y}$ — estimated standard deviation of the scatter around the regression straight line, s_a — estimate of the standard deviation of the shift a, s_b — estimate of the standard deviation of the regression coefficient b.

A study of interferents indicated that Na$^+$, K$^+$, and Cl$^-$ ions do not interfere, Ba^{2+}, Ca^{2+}, and SO$_4^{2-}$ ions do not interfere up to a ratio of 1 : 2000, Zn^{2+}, Mn^{2+}, Ni^{2+}, NO$_3^-$ ions up to a ratio of 1 : 1000, Co^{2+}, Mg^{2+} up to a ratio of 1 : 500, Cu^{2+}, Al^{3+}, Cd^{2+}, and NO$_2^-$ up to a ratio of 1 : 100 and Ru^{3+}, Pt^{4+}, Ir^{4+}, and Pd^{2+} ions up to a ratio of 1 : 5.

Procedure

A gold solution is pipetted into a 25 cm^3 volumetric flask to give a final concentration of up to 10.0 µg cm^{-3}. The acidity is adjusted to pH $\sim$0.7 with a 1 mol dm^{-3} HCl solution, 1.5 cm^3 of 5×10^{-3} mol dm^{-3} Septonex solution is added and the solution is diluted with distilled water to a volume of 25 cm^3. The

solution absorbance must be measured up to 60 min after mixing at a wavelength of 332 nm.

Determination of gold in sample

The proposed method was tested on samples containing gold as the cyanide complex. This complex was converted to the $[AuCl_4]^-$ complex anion by reducing to the metal (using granulated zinc and concentrated HCl) and dissolving, as described under the preparation of the stock gold solution.

Table 2

Determination of gold in sample

Method	Au(III) $\mu g\ cm^{-3}$	
AAS	84.5	84.2
Method proposed	84.1	84.0
	84.0	84.0

Content of gold before reduction was 84.8 $\mu g\ cm^{-3}$ (AAS).

The results of three measurements were compared with those obtained by the atomic absorption spectroscopic method (AAS). The results are given in Table 2.

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