

DYNAMIC SORPTION AND DESORPTION OF GOLD USING SPHERON DEAE AS SORBENT

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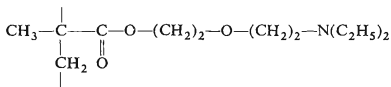
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The dynamic sorption and desorption of gold was studied using Spheron DEAE, a macroreticular hydroxyethyl methacrylate-ethylenedimethacrylate copolymer with chemically bonded diethylaminoethyl groups, as the sorbent. Factorial experiments were designed to optimize the composition of the mobile phase (H^+ and Cl^- ions); as a result, hydrochloric acid was used in a concentration of 0.01 mol l^{-1} . Thiourea solution (0.4 mol l^{-1}) in $0.25M$ hydrochloric acid served as the eluent: the gold sorbed was eluted completely in seven column volumes. A column of 1 cm^3 volume retained gold quantitatively from 0.5 l of solution containing the metal in a concentration of 1 mg l^{-1} ($5 \mu\text{mol l}^{-1}$); the recovery of gold by elution was 99% and the degree of concentration of gold with respect to the influent was a hundred. A method is worked out for a direct photometric determination of gold in the thiourea eluates, based on the decomposition of thiourea with hydrogen peroxide.

Gold in hydrochloric acid solutions can be separated on cellulose-based weakly basic ion exchangers modified by diethylaminoethyl groups. In this way, Kuroda and Yashikuni¹ were able to separate gold from Fe, Co, Ni, Cu, and Zn, present in a twothousandfold mass excess. The distribution coefficient of gold was observed to decrease with increasing concentration of chloride. More recently, Kawabuchi and Kuroda² found that the distribution coefficient of gold in chloride solutions can be raised by adding acetic acid, and made use of this fact for separating gold from platinum metals³. Pohlandt⁴ suggested that methanol and dilute hydrochloric acid can serve as a suitable medium for the sorption of gold on a cellulose sorbent of this kind.

Cellulose sorbents are so far inapplicable to high performance liquid chromatography at medium or high pressures. We investigated⁵ therefore the sorption properties of Spheron DEAE, a hydroxyethylmethacrylate-ethylenedimethacrylate copolymer modified by diethylaminoethyl groups, containing the same weakly basic groups as the cellulose sorbents mentioned, *viz.*



We found that the distribution coefficient of gold is two orders of magnitude higher than the distribution coefficients of some common metals (Zn, Ni, Cu, Co, Fe) and that it increases with diminishing concentration of chloride.

Since previously⁵ we studied the sorption of gold in static conditions only and paid little attention to its desorption, we concentrated now on the dynamic sorption and desorption of gold using the above sorbent. For a direct photometric determination of gold in the eluate containing an excess of interfering thiourea, we suggest a method in which the latter is decomposed prior to the measurement.

EXPERIMENTAL

Chemicals and Apparatus

Solutions of gold were prepared by dissolving the pure metal (Safina, Vestec) in *aqua regia* and evaporating the solution repeatedly to dryness with additions of hydrochloric acid. The chloroauric acid obtained was dissolved in 0.5M-HCl. Spheron DEAE 1000 (Lachema, Brno), particle size 0.063–0.100 mm, theoretical exchange capacity (calculated based on the determined content of nitrogen) $Q_g(N) = 1.27$ mmol per g of dry sorbent, was recycled twice with 2M-NaOH, 2M-NaCl, and 2M-HCl (the sorbent was always washed with water between the use of these agents).

The desorption of gold was accomplished by employing a solution of thiourea⁶ (0.4 mol l^{-1})¹ in hydrochloric acid (0.25 mol l^{-1}).

The absorption spectra were scanned on a Specord UV-VIS spectrophotometer, the photometric measurements were carried out on a VSU-2P instrument (both Carl Zeiss, Jena).

Working Procedures and Analytical Methods

For the static sorption and desorption experiments, 50 mg of sorbent dried in air were equilibrated on a horizontal shaking machine, with 10 ml of solution containing 25 $\mu\text{mol Au}$ and a preselected amounts of hydrochloric acid. The water content in the sorbent dried in air was about 5% as determined by drying it in vacuum over P_2O_5 at 78°C.

The dynamic sorption experiments were conducted in columns with an inner diameter of 4 mm and containing the sorbent in a total volume of 1 cm^3 . The flow rate was adjusted to $F_m = 0.6 \text{ ml} \cdot \text{min}^{-1}$ (hence, to a specific load of $s = 36 \text{ h}^{-1}$); however, owing to the change in the sorbent volume during the sorption and desorption, the flow rate fluctuated between 0.5 and 0.7 ml min^{-1} . Preselected volumes of the effluent were collected and the content of gold in them was determined spectrometrically. In the chloride solutions, gold was determined by a method based on the light absorption by the AuCl_4^- complex⁷. The calibration dependences were measured at 314 nm in 1 cm cells for chloride concentrations of 0.1 and 0.5 mol l^{-1} ; the two plots were identical, hence, the absorbance of the complex at the wavelength used is independent of the chloride concentration in the concentration region mentioned.

In the solutions obtained on the elution of gold with thiourea, the metal was determined by the method described below.

RESULTS AND DISCUSSION

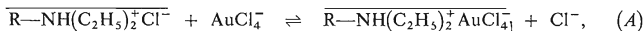
In agreement with the data¹, we have found⁵ that the distribution coefficient of gold,

$$D_g = \eta(\text{Au})_r / c(\text{Au})_{\text{aq}} \quad (I)$$

(η is the content of substance in mol g^{-1} , c is the concentration of substance in $\text{mol} \cdot \text{l}^{-1}$; the subscripts r and aq refer to the exchanger phase and the aqueous phase, respectively), increases with the decreasing concentration of chloride down to the lowest value tested, 0.1 mol l^{-1} (HCl).

Prior to the dynamic tests, we applied the static approach to seek for the optimum composition of the aqueous phase leading to the maximum D value and, consequently, the highest separation recovery R . A 2^2 factorial experiment with double repetition was designed to find that both of the factors examined, $c(\text{H}^+)$ and $c(\text{Cl}^-)$, as well as their interactions are significant. The value that previously⁵ emerged as the optimum, $c = 0.1 \text{ mol l}^{-1}$, was now chosen as the upper limit for the two factors. The distribution equilibrium established rapidly and the maximum sorption-desorption recovery ($R \approx 0.95$) was reached as early as the first sampling (in 10 min). The optimum concentrations of the H^+ and Cl^- ions at which the R value is at its maximum then were sought by a 3^2 factorial design with double repetition. The equation describing the response surface for the factors examined was set up by calculation⁸ and the optimum values of the factors then were found by mapping this surface. As it emerged, the optimum values were the lowest concentrations applied, viz. $c(\text{H}^+) = 5 \text{ mmol} \cdot \text{l}^{-1}$, $c(\text{Cl}^-) = 7 \text{ mmol l}^{-1}$. As the diagram⁹ of the predominating Au(III) species in the presence of Cl^- and OH^- ions shows, the prevailing form of gold is AuCl_4^- even at so low concentrations of H^+ and Cl^- ions. For practical reasons, namely, to prevent the gold from reduction by dust particles, a concentration of hydrochloric acid of 0.01 mol l^{-1} was actually chosen. This has no major effect on the R value, the response surface displaying a small ascent in the neighbourhood of the maximum.

In view of the significance of the concentrations of both chloride ions and protons as factors affecting the distribution coefficient of gold, the sorption mechanism is probably the ion exchange



as is also the case with the chloro complexes of platinum metals¹⁰.

The dynamic sorption and desorption of gold was investigated as follows: A solution of gold (0.01 mol l^{-1}) in 0.01M-HCl was allowed to pass the column until the concentration of gold in the eluate became equal to that in the influent. The column then was washed with five column volumes of water and the gold sorbed was eluted. At the beginning of the elution a white precipitate formed in the mobile phase, bringing about a reduction in the initial flow rate; a steady state established after the passage of four column volumes of the eluent.

During the elution with thiourea, AuCl_4^- is reduced to AuCl , sulphur appears¹¹, and the aurous chloride is transformed by the excess thiourea into the $\text{Au}(\text{SCN}_2\text{H}_4)^+$ complex involving univalent gold¹².

The sorption and desorption breakthrough curves of gold, obtained in the above conditions, are shown in Figs. 1 and 2. The sorption break-through curve was evaluated to afford the breakthrough capacity of the sorbent for gold, 1.16 mmol per g of dry substance, and the total (practical) capacity, 1.37 mmol Au. A comparison of the latter value with the theoretical capacity 1.27 mmol indicates that in addition to the ion exchange, some other mechanism operates in the sorption. Similar dif-

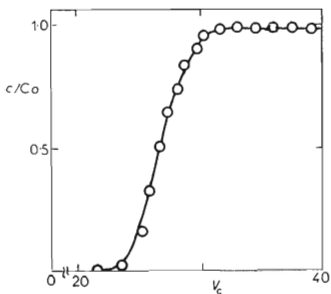


FIG. 1

Sorption break-through curve of gold on Spheron DEAE. Inner diameter of the column $d_i = 4$ mm, $V_c = 1$ cm³, $c(\text{HCl}) = 0.01$ mol l⁻¹, specific load $s = 36$ h⁻¹; c , c_0 concentrations of gold in the effluent and in the influent, respectively

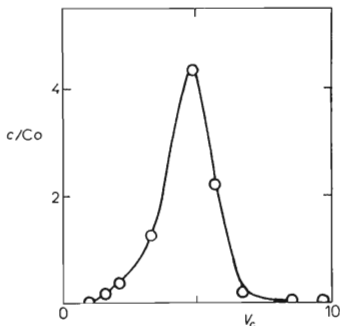
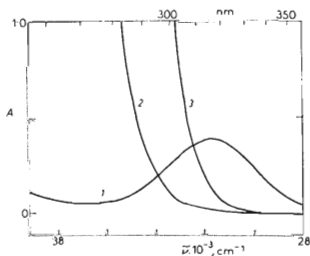


FIG. 2

Desorption break-through curve of gold for Spheron DEAE 1000. $d_i = 4$ mm, $V_c = 1$ cm³, eluting agent: thiourea (0.4 mol . l⁻¹) in 0.25M-HCl; c , c_0 concentrations of gold in the effluent and in the influent, respectively

FIG. 3
Light absorption curves: 1 AuCl_4^- ; $c(\text{Au}) = 76$ $\mu\text{mol l}^{-1}$, $c(\text{HCl}) = 0.1$ mol l⁻¹; 2 complex of gold with thiourea; $c(\text{Au}) = 76$ $\mu\text{mol l}^{-1}$, $c(\text{thiourea}) = 0.4$ mol l⁻¹, $c(\text{HCl}) = 0.25$ mol l⁻¹; 3 thiourea in HCl; $c(\text{thiourea}) = 0.4$ mol l⁻¹, $c(\text{HCl}) = 0.25$ mol l⁻¹. Cell thickness 1 cm, reference solution: HCl (c , mol l⁻¹): 1 0.1, 2, 3 0.25



ferences between the theoretical and the practical capacities have been observed in experiments with sorbents in which the functional group in question was bonded to a different polymeric matrix (cellulose and a glycidyl methacrylate–ethylenedimethacrylate copolymer¹³), and in static sorption experiments⁵. The exchange capacities also indicate that the accessibility to all the exchange groups within a grain of the sorbent is very good. Since – as has been proved by specific surface area measurements on the dried sorbents in the chloride form as well as by the agreement with the results arrived at by other authors¹⁴ – drying of sorbents of this kind results in the formation of compact aggregations with nearly zero total pore volume, the pores obviously must be made open when the sorbent swells up.

The sorption of gold and its desorption with the thiourea solution was repeated, and no change in the exchange capacity was observed even after 25 cycles. A sevenfold column volume was sufficient for a complete desorption of gold. The possibility of using the sorbent, Spheron DEAE, for a pre-concentration of gold from aqueous solutions was also tested. A volume of 0.5 l of solution containing gold in a concentration of $5 \mu\text{mol l}^{-1}$ (hence, about 1 mg l^{-1}) was passed through a column of 1 cm^3 of sorbent to achieve a hundredfold degree of concentration with a recovery of 99%.

Initially, we determined gold in the thiourea eluates gravimetrically after decomposing the thiourea complex in alkaline medium⁶. A direct photometric measurement was hampered by the fact that at the wavelength of the maximum absorbance of the chloro complex of gold (314 nm), thiourea interferes badly, and exhibits a high absorbance also at shorter wavelengths, in the range where the thiourea complex of gold could manifest itself (Fig. 3). Now, we circumvented this difficulty by oxidizing the thiourea with hydrogen peroxide¹⁵; this reaction proceeds completely (*i.e.*, to such a degree that as a result, zero absorbance is measured at 314 m) only if hydro-

TABLE I

Accuracy of the determination of gold after the decomposition of its thiourea complex

Au added mg l^{-1}	Au found ^a , mg l^{-1}	
	A ^b	B ^b
20.50	20.51	20.51
16.41	16.40	16.43
11.73	11.72	11.76

^a Average of duplicate determinations; ^b A in the absence of thiourea, B after the decomposition of thiourea with hydrogen peroxide.

chloric acid is added to the thiourea before the hydrogen peroxide, the mixture is allowed to stand for a while, and then brought to boil. By adding two volumes of concentrated HCl and one volume of 30% H_2O_2 to one volume of 0.4M thiourea, the thiourea complex of gold can be decomposed in this manner too. After the decomposition, the chloride concentration must be adjusted to lie within the region of validity of the calibration plot (hence, $c(\text{HCl}) = 0.1 - 0.5 \text{ mol l}^{-1}$). The accuracy of the determination of gold by the photometric method after the decomposition of thiourea with hydrogen peroxide is documented by Table I.

The two sets of data were compared by applying the Student test¹⁶; the obtained value of $t = 1.597$ is lower than $t_\alpha = 2.571$ for $\alpha = 0.05$ and $\nu = 5$, showing that the two series coincide. The reproducibility of determination, expressed as the relative standard deviation calculated for a series of duplicate measurements on 10 samples, was $s_r = 0.63\%$.

A sufficient selectivity of Spheron DEAE to gold in the presence of some common metals has been demonstrated previously⁵; in view of the present work, the sorbent appears suitable also for a dynamic separation and preconcentration of gold.

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