HPLC OF PLATINUM METALS AND GOLD BASED ON THEIR BROMO COMPLEXES

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$Pt^{II,IV}$, Pd^{II}, and Au^{III} can be separated and quantitated by HPLC in the form of ion-associates of their bromo complexes with the cetyltrimethylammonium (CTMA) cation, using the acetonitrile–water 60 : 40 system containing 0.002 mol l^{-1} CTMA and 0.05 mol l^{-1} NaBr (pH 3) as the mobile phase and detection at 240 nm. In such circumstances the detection limits for the injection of 20 μl sample are 6.7, 0.4, 0.9, and 4.3 ng for Pt^{II}, Pt^{IV}, Pd^{II}, and Au^{III}, respectively. Excess Fe^{3+}, Al^{3+}, Mg^{2+}, Ca^{2+}, NO_3^-, SO_4^{2-}, and Cl^- does not interfere. On-line preconcentration of the $Pt^{II,IV}$ bromo complexes on Separon SGX RPS is recommended.

Key words: Chromatography; Platinum metals; Gold; Bromo complexes; Preconcentration.

Analytical chemistry of platinum metals, platinum in particular, calls attracting attention due to the potential toxicity of this metal in the environment and also in view of the necessity of controlling the platinum content of body fluids during the therapy of some forms of cancer. The analytical reactivity of platinum metals (except for Pd^{II}) in halide solutions is adversely affected by its rather complex kinetics: the equilibrium establishes slowly and often only at elevated temperatures approaching the boiling point.

The HPLC method with various detection techniques has been applied to the separation and quantitation of pharmaceuticals which are based on Pt^{II} and their biotransformation products[1–5], separation of ion-associates of EDTA chelates of Pd^{II} and Pt^{II} in platinum concentrates[6], and separation of platinum metal complexes with *N*-heterocyclic azodyes[7–10].

Separation of platinum metal and gold chloro complexes in the form of their ion-associates was only successful for Au and Pd with the tetramethylammonium cation in the mobile phase, using a sorbent based on a chemically modified C18 silica gel (ref.[11]), and for Ir^{IV}, Os^{IV}, and Pt^{IV} using a perchlorate-containing mobile phase and a strongly basic anion exchanger based on chemically modified silica gel[11].

This paper describes separation of Pt^{II}, Pt^{IV}, Pd^{II}, and Au^{III} on the basis of ion-associates of their bromo complexes with the cetyltrimethylammonium cation in the presence of bromide in the mobile phase, using a chemically modified C18 silica gel and detection in the UV spectral region. Such procedure is also suitable for the on-line preconcentration of platinum.

EXPERIMENTAL

Apparatus

The analyses were performed on a homemade liquid chromatograph interfaced to a Varian 8500 pump and an LCD 2040 photometric detector (Laboratorni pristroje, Prague, Czech Republic). A PU 4021 diode array detector (Pye Unicam, U. K.) was also employed. Samples were injected by means of an LCP 4000 pump (preconcentration) or an LCI 30 loop injector with a 20 μl loop (both Ecom, Prague, Czech Republic). Gilson micropipettes 200 and 1 000 μl volume were used for pipetting. The pH was measured with an OP 208/1 pH-meter interfaced to an OP 0808P combined electrode (Radelkis, Hungary), calibrated by using standard NBS buffers pH 4.00 and pH 7.00 at 25 °C. The reported pH values of the mobile phases refer to the pH of the aqueous solutions; no corrections were made for the presence of the organic component. The spectra were measured on a Specord M 40 double-beam spectrophotometer (Zeiss, Jena, Germany).

Columns and Stationary Phase

Analytical column: 150 × 3 mm, packed with Separon SGX-RPS 7 μm. Sorption precolumn: 30 × 3 mm, packed with Separon SGX-RPS 60 μm (all Tessek, Prague, Czech Republic).

Mobile Phase

The methanol–water or acetonitrile–water systems containing ingredients were degassed in an ultrasonic bath for 10 min. The flow rate through the column (150 × 3 mm) was 0.5 ml min^{-1}. The mobile phase compositions as reported further in the text are in volume proportions.

Chemicals

The solution of $[PtCl_6]^{2-}$ was prepared by dissolving 1.9233 g of the pure metal (Safina, Prague, Czech Republic) in 10 ml of a mixture of concentrated HCl and HNO_3 (3 : 1) and evaporating to dryness. Evaporation with 1 ml of concentrated HCl was repeated three times and finally, HCl was added in an amount such that its concentration in the final volume of 100 ml was 0.2 mol l^{-1}.

The solution of $[PtCl_4]^{2-}$ was prepared by heating 5.2 ml of the stock solution of $[PtCl_6]^{2-}$ with 1.64 ml of a 0.8% solution of hydrazine hydrate to 40 °C and diluting with 0.2 mol l^{-1} HCl to a final volume of 100 ml. The resulting concentration was 1 000 ppm.

Solution of $[PdCl_4]^{2-}$ at a concentration of 26.58 mg Pd ml^{-1} was obtained by dissolution of analytical grade $PdCl_2$ in 0.2 mol l^{-1} HCl and standardized gravimetrically using nioxime[12].

Solutions of Rh (2 mg ml^{-1}) and Os and Ir (0.2 mg ml^{-1}) were prepared by dissolving $(NH_4)_3RhCl_6 \cdot 1.5\ H_2O$, $(NH_4)_3OsCl_6$, and $(NH_4)_3IrCl_6 \cdot H_2O$, respectively (all specpur, Johnson, Matthey, London, U. K.), in 0.2 mol l^{-1} HCl.

Solution of Ru (1 mg ml^{-1}) was obtained by alkali-oxidizing fusion of the pure metal with Na_2O_2 and dissolution of the melt in HCl to a resulting concentration of approximately 0.2 mol l^{-1}.

Solution of $[AuCl_4]^-$ at a concentration of 9.9 mg Au ml^{-1} was prepared by dissolving anhydrous $AuCl_3$ (Safina, Prague, Czech Republic) in HCl to a resulting concentration of 0.2 mol l^{-1}. The solution was standardized gravimetrically as Au (ref.[13]).

Platinum metal and gold bromo complexes were synthesized from the stock solutions of the chloro complexes by heating with 46% HBr (reagent grade purity) to boil; only for Rh, Os, and Ir, their salts were directly employed. After dilution with water to the final volume, the metal concentration was 0.2 mg ml^{-1} and the HBr concentration was 0.2 mol l^{-1}.

For on-column injection, the solutions were diluted with redistilled water in the presence bromide so that the concentration of the latter in the final solution was of 0.1 mol l^{-1}.

The standard solutions of the remaining metals were prepared from the pure metals or nitrates and standardized by EDTA titration. Tetramethylammonium bromide (TMA), tetrabutylammonium hydroxide (TBA), cetyltrimethylammonium bromide (CTMA), and methanol (Lachema, Czech Republic), which were added to the mobile phase, were of reagent grade purity; acetonitrile (Merck, Germany) was of chromatographic purity.

All solutions were made up using redistilled water, prepared in a quartz still (Heraeus, Germany).

Calibration

Calibration curves were constructed based on the peak heights applying linear regression methods. The sensitivity of the signals was characterized by the calibration straight line slope. The detection limit was calculated as the analyte concentration whose signal corresponded to the triple baseline noise.

On-line Sorption of the Pt^{II,IV} Bromo Complex on the Precolumn

The sorption was performed from 10 (100) ml of sample containing 1 to 25 ppb Pt^{II,IV} at the optimum sample composition, *i.e.* 5% acetonitrile with 0.01 mol l^{-1} Br^{-} at pH 3. The flow rate was 9.9 ml min^{-1}. After flushing for 20 s with 3.3 ml of the mobile phase, which was the acetonitrile–water 60 : 40 mixture containing 0.002 mol l^{-1} CTMA and 0.05 mol l^{-1} NaBr at pH 3, the injection valve was switched to empty the precolumn in the counter-current mode onto the analytical column (Fig. 1). The injection pump was then flushed with water.

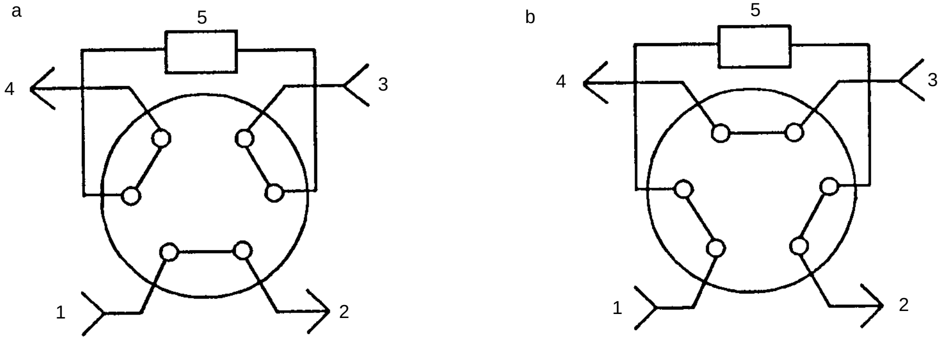

FIG. 1

Layout for the on-line preconcentration and subsequent HPLC quantitation: 1 mobile phase, 2 analytical column, 3 sample, 4 waste, 5 precolumn; a injection valve position during chelate sorption on precolumn, b countercurrent elution of the precolumn

RESULTS AND DISCUSSION

Spectrophotometric Properties of the Chloro and Bromo Complexes of $Pt^{II,IV}$, Pd^{II}, Au^{III}, Ir^{III}, Os^{IV}, Rh^{III}, *and* Ru^{III}

For the Pt^{IV} and Pd^{II} chloro complexes, the literature reports absorption maxima at 262 nm ($[PtCl_6]^{2-}$) and 221 and 281 nm ($[PdCl_4]^{2-}$), respectively, with molar absorptivities lying within the region of 4 000–22 000 mol l^{-1} cm^{-1} in dependence on the wavelength and concentration of free chloride in the solution. For $[PtCl_4]^{2-}$ and $[AuCl_4]^{-}$ the absorption maxima lie at 212 and 226 nm, respectively[14–18].

For the bromo complexes, the absorption peaks are shifted towards the visible region: *e.g.*, 247 and 330 nm for $[PdBr_4]^{2-}$, 263 nm for $[PtBr_4]^{2-}$, and 254 nm for $[AuBr_4]^{-}$ (refs[17,18]).

Mixed halo complexes of platinum metals where some halide ligands are substituted by OH^-, H_2O, or other ligands present in the solution are assumed to occur in solutions where halide fails to be present in a sufficient excess; for instance, $[PtCl_6]^{2-}$ is accompanied by 20% $[PtOHCl_5]^{2-}$ in a solution containing chloride at a concentration of 0.05 mol l^{-1} (ref.[17]).

Spectrophotometric data of some halo complexes of platinum metals and gold are incomplete or lacking altogether: this applies, for example, to the chloro complexes of Os and Ir and bromo complexes of Pt^{IV}, Ru, Os, Ir, and Rh.

In the present work, the dependence of the absorption spectra of Pd^{II}, Pt^{II}, Pt^{IV}, and Au^{III} chloro complexes on the concentration of chloride was measured across the region of 0.1–4 mol l^{-1} Cl^- at a constant acidity (0.01 mol l^{-1} HCl), and the dependence on the hydrogen ion concentration was measured across the region of 0.001–1 mol l^{-1} H^+ at a constant concentration of chloride (1 mol l^{-1} NaCl). The absorbance over the 210–400 nm region was independent of the hydrogen ion concentration and, except for the Pd^{II} chloro complex, independent of the chloride ion concentration as well. For the Pd^{II} chloro complex, the absorbance in the absorption peak region increased with increasing chloride concentration, to be 50% higher at 1 mol l^{-1} Cl^- than at 0.1 mol l^{-1} Cl^-. The absorption spectra of Pd^{II}, Pt^{II}, Pt^{IV}, Au^{III}, Ir^{III}, Os^{IV}, Rh^{III}, and Ru^{III} are shown in Fig. 2.

As with the chloro complexes, the absorption spectra of the $Pt^{II,IV}$, Pd^{II}, and Au^{III} bromo complexes, measured over the 235–500 nm region, were independent of the hydrogen ion concentration (0.001–1 mol l^{-1}) at a constant concentration of bromide (0.01 mol l^{-1} NaBr). Independence on the bromide concentration (0.01–4 mol l^{-1}), however, was only found for the Au^{III} bromo complex, whereas for the remaining complexes, a marked absorbance decrease at bromide concentrations lower than 0.1 mol l^{-1} in comparison with 0.01 mol l^{-1} NaBr was observed for Pt^{IV} (8%), Pt^{II} (7%), and Pd^{II} (40%). The absorption spectra of bromo complexes of $Pt^{II,IV}$, Pd^{II}, Au^{III}, Ir^{III}, Os^{IV}, Rh^{III}, and Ru^{III} are shown in Fig. 3.

So, it is clear that within the region examined, the concentration of hydrogen ions does not affect the spectral characteristics of the complexes of $Pt^{II,IV}$, Pd^{II}, or Au^{III}. The dependence on the ligand concentration is most marked for the least stable Pd^{II} complexes.

For the bromo complexes of the above three metals in the presence of 0.1 mol l^{-1} NaBr and 0.005 mol l^{-1} HBr, the presence of CTMA at 0.0025 mol l^{-1} brings about a 10% decrease in the Au^{III} peak absorbance; TBA (0.01 mol l^{-1}) reduces the absorbance by 6 and 10% for the Au^{III} and Pd^{II} complexes, respectively; and 90% acetonitrile lowers the absorbance of the Pt^{IV} and Pd^{II} bromo complexes by 30 and 10%, respectively. Moreover, for all of the bromo complexes, acetonitrile causes a 2–3 nm shift towards longer wavelengths.

The absorption characteristics of the chloro and bromo complexes of $Pt^{II,IV}$, Pd^{II}, and Au^{III} are compared in Table I. The table shows that for those metals, the bromo complexes are better suited to the separation and HPLC determination with spectrophotometric detection than the chloro complexes: their colour contrast and sensitivity are higher, and the bromo complexes are also better stable[19].

Following column separation using the acetonitrile–water 60 : 40 system containing 0.002 mol l^{-1} CTMA and 0.05 mol l^{-1} NaBr at pH 3 as the mobile phase, the absorption

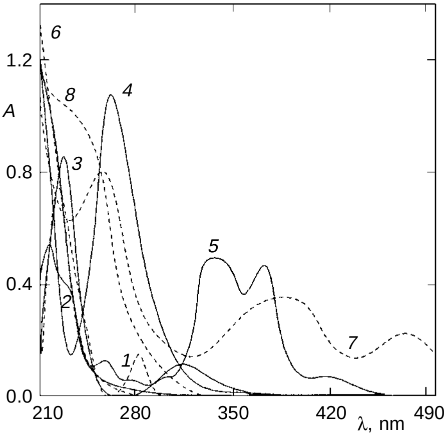

FIG 2
Absorption spectra of Pd^{II} (*1*), Pt^{II} (*2*), Au^{III} (*3*), Pt^{IV} (*4*), Os^{IV} (*5*), Ir^{III} (*6*), Ru^{III} (*7*), and Rh^{III} (*8*) chloro complexes in water containing 0.01 mol l^{-1} NaCl and 0.001 mol l^{-1} HCl (against pure water). Mass concentrations (mg l^{-1}): *1*, *7*, *8* 5; *2*, *5*, *6* 10; *3* 4.5; *4* 9. Lines: *1*, *6*, *7*, *8* dashed; *2*, *3*, *4*, *5* solid. Free ligand absorbance is negligible

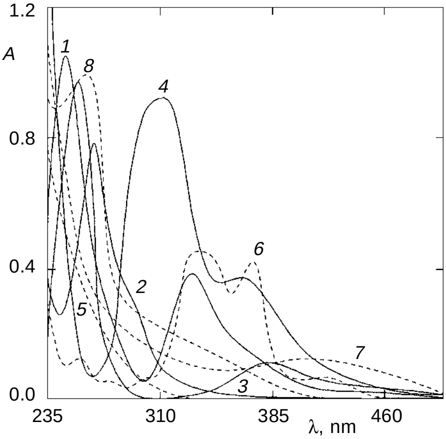

FIG. 3
Absorption spectra of Pd^{II} (*1*), Pt^{II} (*2*), Au^{III} (*3*), Pt^{IV} (*4*), Os^{IV} (*5*), Ir^{III} (*6*), Ru^{III} (*7*), and Rh^{III} (*8*) bromo complexes in water containing 0.1 mol l^{-1} NaBr and 0.01 mol l^{-1} HBr (against pure water). Mass concentrations (mg l^{-1}): *1* 4; *2* 20; *3*, *8* 5; *4*, *5*, *6*, *7* 10. Lines: *1*, *2*, *3*, *4* solid; *5*, *6*, *7*, *8* dashed. Free ligand absorbance is negligible

spectra of the platinum metal and gold bromo complexes were measured with the diode array detector (Table II, Fig. 4).

For HPLC it is relevant that all of the bromo complexes absorb intensely at 240 nm. This wavelength is well suited to the detection of the complexes after their mutual separation, although the background absorbance due to bromide in the mobile phase increases.

TABLE I
Comparison of absorption characteristics of $Pt^{II,IV}$, Pd^{II}, and Au^{III} chloro and bromo complexes

Metal	λ_{max}, nm		Δ^a, nm		A^b	
	Cl	Br	Cl	Br	Cl	Br
Pt^{II}	216	267	10	35	0.28	0.40
Pt^{IV}	262	313	56	81	0.60	0.46
		365		133		0.19
Pd^{II}	223	247	17	15	1.12	1.30
	281	332	75	100	0.32	0.48
Au^{III}	227	255	21	23	0.94	0.97
	314	382	108	150	0.13	0.12

[a] $\Delta = \lambda_{max} - \lambda_0$ where λ_0 is the wavelength at which the molar absorptivity of the ligand equals 1 ($\lambda_{0,Br}$ = 232 nm, $\lambda_{0,Cl}$ = 206 nm); [b] absorbance of the complex at λ_{max} at a metal concentration of 5 ppm and ligand concentration 0.1 mol l^{-1}.

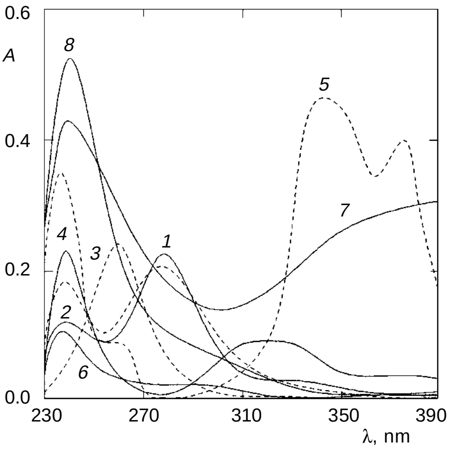

FIG. 4
Absorption spectra of Pd^{II} (*1*), Pt^{II} (*2*), Au^{III} (*3*), Pt^{IV} (*4*), Os^{IV} (*5*), Ir^{III} (*6*), Ru^{III} (*7*), and Rh^{III} (*8*) bromo complexes after column separation. Mass concentration of metal in sample injected: 16 mg l^{-1}, mobile phase: acetonitrile–water 60 : 40 (vol.%) mixture containing 0.002 mol l^{-1} CTMA and 0.05 mol l^{-1} NaBr at pH 3, detection with a diode array detector. For the dashed lines the absorbances are 10-fold lower

Conditions for HPLC Separation of Pd^{II}, Pt^{IV}, Pt^{II}, and Au^{III}

The effects of the kind and concentration of the ion pairing agent, organic solvent, salts, and mobile phase pH on the retention of the bromo complexes were investigated.

Effect of Organic Solvent in the Mobile Phase on the Retention Times of the Pt^{II,IV}, Pd^{II}, and Au^{III} Bromo Complexes

When using the methanol-containing mobile phase (methanol–water 80 : 20 with 0.002 mol l^{-1} CTMA and 0.05 mol l^{-1} NaBr at pH 3), the elution order was nearly reverse in comparison with that observed when using the acetonitrile-containing mobile phase (acetonitrile–water 60 : 40 with 0.002 mol l^{-1} CTMA and 0.05 mol l^{-1} NaBr, pH 3):

methanol: Au^{III} < Pt^{IV} < Pd^{II} < Pt^{II},
acetonitrile: Pd^{II} < Pt^{II} < Pt^{IV} < Au^{III}.

While the proton acceptor mechanism predominates with methanol, the dipole–dipole interaction prevails with acetonitrile (the CTMA cation solvates well). Acetonitrile emerged as more suitable particularly owing to the shorter retention times of the low stability Pd^{II} and Pt^{II} complexes: their peaks do not tail when using the 60% acetonitrile mobile phase and their determination is more sensitive, particularly for the Pd^{II} bromo complex.

The dependence of the retention times on the acetonitrile concentration in the mobile phase is shown in Fig. 5.

Effect of the Ion Pairing Agent in the Mobile Phase

Irrespective of the kind of the ion pairing agent, its increasing concentration in the mobile phase brings about increase in the retention times of the complexes. For the short-chain ion pairing agents TMA and TBA, only 20 and 45% organic solvent, respectively, was used in the mobile phase and their concentration in it was roughly tenfold with respect to the longer-chain ion pairing agent (CTMA).

The elution order depends on the ion pairing agent as follows:

TMA: Pt^{II} < Pt^{IV} < Pd^{II} < Au^{III},
TBA: Pt^{II} < Pd^{II} < Pt^{IV} < Au^{III},
CTMA: Pd^{II} < Pt^{II} < Pt^{IV} < Au^{III}.

TABLE II
Absorption maxima of the bromo complexes after HPLC separation. Mobile phase: acetonitrile–water 60 : 40 containing 0.002 mol l^{-1} CTMA and 0.05 mol l^{-1} NaBr at pH 3; measurement with a diode array detector

Metal	Pt^{II}	Pt^{IV}	Pd^{II}	Au^{III}	Ir^{III}	Os^{IV}	Rh^{III}	Ru^{III}
λ_{max}, nm	238 275	239 320	238 277	260	237 286	237 345	242	240 >390

These series indicate that with shorter-chain ion pairing agents the retention times of the Pd^{II} bromo complex grow longer.

CTMA at the optimum concentration of 0.002 mol l^{-1} was chosen with regard to the more sensitive determination of Pd^{II}. The dependences of the retention times on the CTMA concentration are shown in Fig. 6.

Effect of Bromide and Mobile Phase pH on the Retention Times of the Pt^{II,IV}, Pd^{II}, and Au^{III} Bromo Complexes

With regard to the lower stability[19] of the Pd^{II} and Pt^{II} bromo complexes, resulting in tailing and peak decrease, it is suitable to add bromide ions to the mobile phase with a view to preventing decomposition of the complexes. The decomposition is especially marked for the Pd^{II} complex if the bromide concentration in the mobile phase is lower than 0.02 mol l^{-1}.

The dependence of the retention times of the complexes on bromide concentration is shown in Fig. 7.

On the other hand, due to the competitive equilibria on the sorbent, the retention times of the complexes decrease with increasing bromide concentration; the Br$^-$ anions displace the anions of the complexes from the sorbent surface. With respect to the practical aspects of the analysis (higher halide concentrations causing corrosion of the

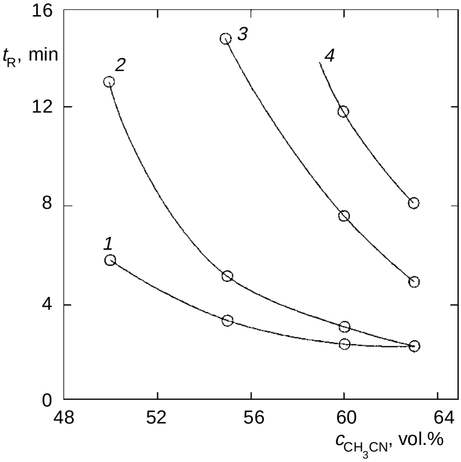

FIG. 5

Dependence of retention times of Pd^{II} (*1*), Pt^{II} (*2*), Pt^{IV} (*3*), and Au^{III} (*4*) bromo complexes on the volume fraction of acetonitrile in mobile phase containing water, 0.002 mol l^{-1} CTMA and 0.1 mol l^{-1} NaBr at pH 3. Stationary phase: Separon SGX RPS (7 μm), column 150 × 3 mm

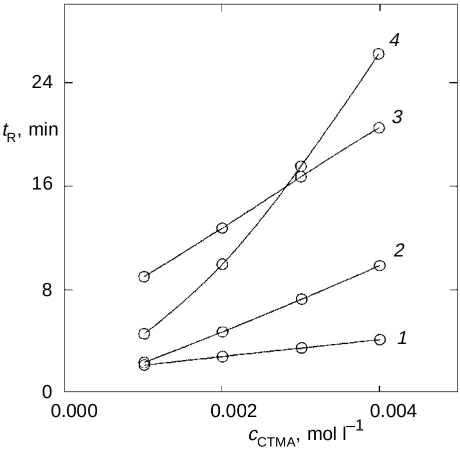

FIG. 6

Dependence of retention times of Pd^{II} (*1*), Pt^{II} (*2*), Au^{III} (*3*), and Pt^{IV} (*4*) bromo complexes on the concentration of CTMA in the mobile phase consisting of the acetonitrile–water 60 : 40 (vol.%) system containing CTMA and 0.1 mol l^{-1} NaBr at pH 3. Stationary phase: Separon SGX RPS (7 μm), column 150 × 3 mm stainless steel components of the chromatographic apparatus) and to the resolution of the peaks, 0.05 mol l^{-1} was chosen as the optimum concentration for bromide.

No dependence of the retention times on the pH was observed within the region of pH 2–4. In subsequent measurements, the acidity was adjusted to pH 3 with HBr.

Optimum Composition of the Mobile Phase

It follows from the data reported above that the optimum mobile phase composition for the separation and quantitation of the bromo complexes of $Pt^{II,IV}$, Pd^{II}, and Au^{III} is as follows: acetonitrile–water 60 : 40 containing 0.002 mol l^{-1} CTMA and 0.05 mol l^{-1} NaBr at pH 3. Typical chromatograms for the three metals are shown in Fig. 8.

Chromatographic Behaviour of Additional Platinum Metals

The chromatographic behaviour of the Ir^{III}, Os^{IV}, Rh^{III}, and Ru^{III} bromo complexes was examined using the optimum mobile phase composition as specified in the preceding paragraph. The retention times are given in Table III.

The table demonstrates that Ir^{III}, Rh^{III}, and Ru^{III} are eluted very close to the dead time (1.3 min) and so they cannot be separated sufficiently in this system. Lowering the

TABLE III
Retention times of Ir^{III}, Os^{IV}, Rh^{III}, and Ru^{III} bromo complexes. Mobile phase as in Table II, stationary phase: Separon SGX RPS (7 µm), column 150 × 3 mm

Metal	Ir^{III}	Os^{IV}	Rh^{III}	Ru^{III}
Retention time, min	1.47	7.43	1.35	1.43

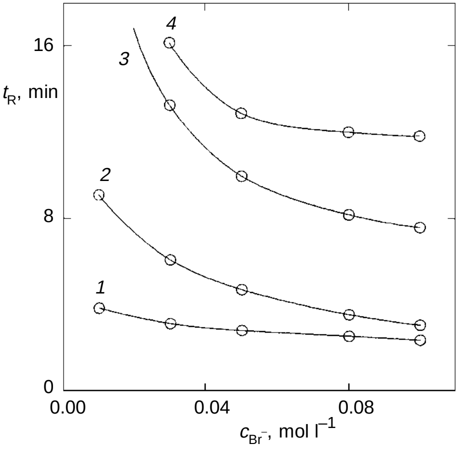

FIG. 7
Dependence of retention times of Pd^{II} (*1*), Pt^{II} (*2*), Pt^{IV} (*3*), and Au^{III} (*4*) bromo complexes on the concentration of bromide (NaBr) in the mobile phase consisting of the acetonitrile–water 60 : 40 (vol.%) system with 0.002 mol l^{-1} CTMA at pH 3. Stationary phase: Separon SGX RPS (7 µm), column 150 × 3 mm

acetonitrile fraction did not improve the result. The composition of three complexes is probably $[Me^{III}Br_6]^{3-}$. (For Ru, its oxidation number and presumed composition of the bromo complex[17] have been deduced from the chromatographic behaviour, which is similar to that of the $[Ir^{III}Br_6]^{3-}$ and $[Rh^{III}Br_6]^{3-}$ complexes.) The high negative charge seems to be responsible for the fast elution of the complexes from the column. Pd, Pt, and Os form another group, where the composition of the complexes will probably be $[PdBr_4]^{2-}$, $[PtBr_4]^{2-}$, $[PtBr_6]^{2-}$, and $[OsBr_6]^{2-}$. These complexes are retained to a larger extent (retention times from 2.4 to 9.5 min). The $[AuBr_4]^-$ complex is retained by the column most, interacting to the highest extent with the CTMA cations presumably owing to its charge of one.

Calibration Curves and Interference

The calibration curves for the $Pt^{II,IV}$ and Pd^{II} bromo complexes were plotted using 5 calibration solutions, applying the optimum mobile phase composition (see above). Each solution contained all the 3 bromo complexes, whose concentrations grew across the 2–10 ppm region in 2 ppm steps. The calibration curve of the Au^{III} bromo complex was measured separately at 260 nm. The calibration plots obtained were linear, with statistical parameters as given in Table IV.

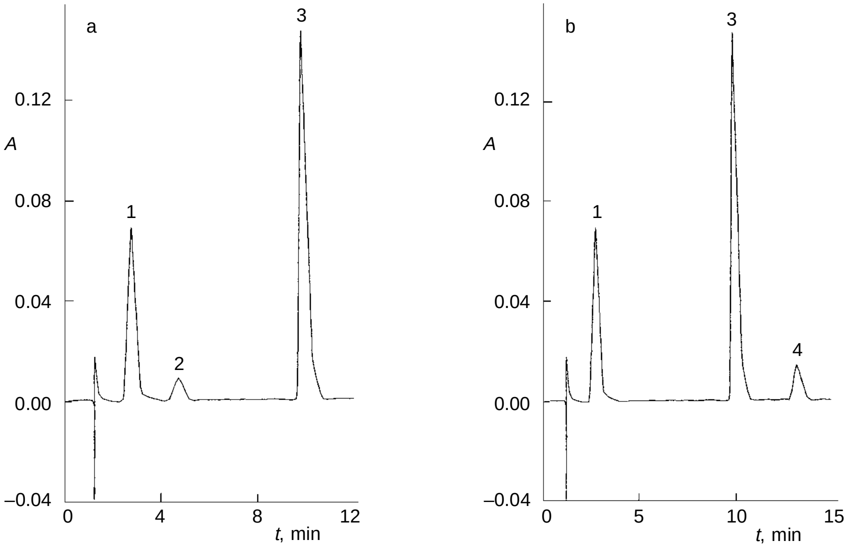

FIG. 8

Chromatograms of Pd^{II} (1), Pt^{II} (2, a), Pt^{IV} (3), and Au^{III} (4, b) bromo complexes. Mass concentration of metal in 20 μl sample injected: 10 mg l^{-1}. Mobile phase: acetonitrile–water 60 : 40 (vol.%) mixture containing 0.002 mol l^{-1} CTMA and 0.05 mol l^{-1} NaBr at pH 3. Stationary phase: Separon SGX RPS (7 μm), column 150 × 3 mm. Detection at 240 nm (260 nm for Au)

Even in a 5 000-fold molar excess, Fe^{3+}, Al^{3+}, Mg^{2+}, or Ca^{2+} did not exert any interfering effect on the retention times and sensitivity of determination of 5 ppm Pd^{II}, Pt^{II}, Pt^{IV}, and Au^{III}.

For anions, competitive complexing equilibria and sorption equilibria on the column can be involved. Neither of the two phenomena, however, played a role in the on-column injection mode. The retention times and sensitivity of determination of Pd^{II}, Pt^{II}, Pt^{IV}, and Au^{III} were unaffected by the presence of nitrate, sulfate, or chloride in a 5 000-fold molar excess.

On-Line Preconcentration of Pt^{II} *and* Pt^{IV}

Effect of Precolumn Flow Rate

When passing a solution containing 50 ppb Pt^{IV} (Pt^{II}), 1% acetonitrile, and 0.05 mol l^{-1} bromide at flow rates from 1 to 9.9 ml min^{-1}, the peak heights of the bromo complexes remained virtually constant; a slight decrease was only observed if the flow rate was lower than 2 ml min^{-1}, presumably due to gradual hydrolysis of the sorbed bromo complexes in the longer times of sorption associated with lower flow rates. This decrease in the concentration of Pt^{IV} bromo complexes with time was confirmed by repeated sorption and injection of 10 ml of a stock solution containing 50 ppb Pt^{IV}, 1% acetonitrile, and 0.05 mol l^{-1} bromide. The time period between the sorptions was 15 min. In each subsequent sorption, the peak of the Pt^{IV} bromo complex was roughly 20% lower than in the preceding cycle. The maximum flow rate of 9.9 ml min^{-1} achievable with the pump was used; this led to the shortest preconcentration times.

So, in order to obtain reproducible results, the preconcentration process should be as fast as possible, adhering to constant time intervals between the operations, from the sample preparation to its on-column injection.

TABLE IV
Statistical parameters of calibration curves of $Pt^{II,IV}$, Pd^{II}, and Au^{III} based on peak heights (in absorbance units)

Metal	a^a, l mol^{-1}	$m_{lim}{}^b$, ng
Pd^{II}	740 ± 30	0.9
Pt^{II}	175 ± 7	6.7
Pt^{IV}	2 870 ± 90	0.4
Au^{III}	278 ± 18	4.3

[a] Calibration dependence slope, $a = \partial A/\partial C \pm ts_a$; [b] detection limit for the injection of 20 µl sample, $m_{lim} = 3s_0M_M\, 2\,.\,10^4/a$; s_0 is the standard deviation of baseline absorbance, $s_0 = 0.0001$. Detection at 240 nm (260 nm for Au^{III}). The calibration dependence intercepts are all statistically insignificant.

Effect of Bromide and Acetonitrile Concentrations in Sample

Excess bromide should be present in sample to slow down hydrolysis of the low concentrations of Pt^{II} and Pt^{IV} bromo complexes. However, competitive desorption of the complexes then takes place on the precolumn and the peak heights on the analytical column decrease (Fig. 9). In view of this, a bromide concentration of 0.01 mol l^{-1} only was employed.

Acetonitrile in the sample solution has a beneficial effect on the sorption properties of the precolumn up to 5–10% contents, whereas at higher concentrations this compound induces elution of the sorbed bromo complexes out of the precolumn. The 5% acetonitrile concentration emerged as optimal.

If, following the preconcentration, the precolumn is rinsed with water only, then a system peak appears in the dead retention volume range after injection of the precolumn content on the analytical column. This peak, whose magnitude is inversely dependent on the detection wavelength, can interfere partly with that of the Pt^{II} bromo complex.

The system peak can be eliminated by flushing the precolumn after preconcentration with the mobile phase so that this liquid fills the precolumn completely. For the facility used, a washing period of 20 s and a flow rate of 9.9 ml min^{-1} appeared suitable (Fig. 10).

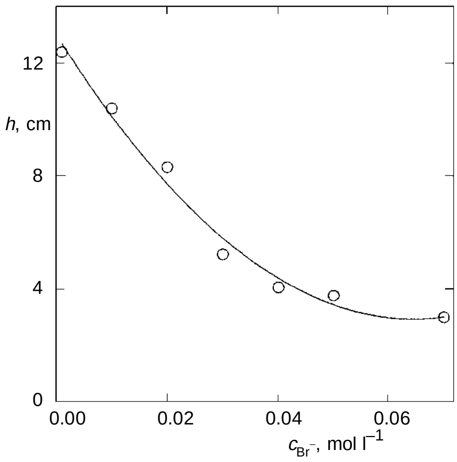

FIG. 9

Dependence of the peak height on the bromide concentration for sample containing 25 μg l^{-1} Pt^{IV} in 1 vol.% acetonitrile at pH 3. Sorption of 10 ml of sample followed by 3.3 ml of the mobile phase, both at a flow rate of 9.9 ml min^{-1}. Detection at 320 nm

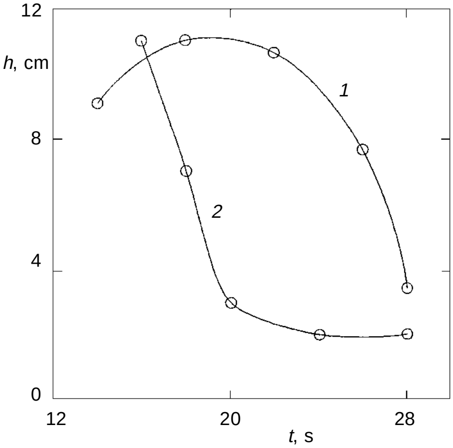

FIG. 10

Dependence of analyte (*1*) and system (*2*) peak heights (in mm) on the time of precolumn elution with the mobile phase. Sample: 10 ml of solution consisting of 25 μg l^{-1} Pt^{IV} in 5 vol.% acetonitrile containing 0.01 mol l^{-1} NaBr at pH 3. Sorption and elution flow rate: 9.9 ml min^{-1}. Detection at 320 nm

In general, the optimum period depends on the capillary and precolumn length and diameter, sorbent kind and grain size, and precolumn flow rate.

Calibration Curve and Effect of Additional Ions During the Preconcentration of $Pt^{II,IV}$ Bromo Complexes

The calibration curve for 5 samples within the Pt concentration span of 1–25 ppb, applying the preconcentration procedure, possesses the following parameters:

for Pt^{IV}: $e = (216 \pm 13) . 10^3$ l mol^{-1}, $m_{\text{lim}} = 2.7$ ng,

for Pt^{II}: $e = (14 \pm 1) . 10^3$ l mol^{-1}, $m_{\text{lim}} = 42$ ng,

where e is the calibration dependence slope ($e = \partial A/\partial C \pm ts_e$), m_{lim} is the detection limit for the sorption of 10 ml sample ($m_{\text{lim}} = 3s_0M_{\text{M}} . 10^7/e$), and s_0 is the standard deviation of the baseline absorbance ($s_0 = 10^{-4}$). The calibration slope intercept is statistically insignificant. The evaluation was based on the peak heights in absorbance units.

Comparison of the calibration dependence slopes applying or omitting the on-line preconcentration (Table IV) reveals that preconcentration brings about a 75-fold to 80-fold sensitivity improvement.

Based on a comparison of the peak areas after the sorption of 10 ml of sample with 20 ppb Pt^{IV} and after the direct injection of 20 μl of sample with 10 ppm Pt^{IV}, the sorption recovery was calculated to be about 20%.

The peak height for sorption from 100 ml of sample with 2 ppb Pt^{IV} is not 10-fold higher than if 10 ml of sample is used; in fact, it is 8% lower, presumably due to gradual hydrolysis.

At a concentration of 25 ppb Pt^{IV}, Fe^{3+} and Al^{3+} do not interfere in a 1 000-fold molar excess and Mg^{2+} and Ca^{2+} do not interfere in a 5 000-fold molar excess.

The effect of anions on the preconcentration is similar to that of the bromide ion (Fig. 9). Chloride induces roughly the same decrease of the $Pt^{IV,II}$ peak as bromide, with nitrate and sulfate the decrease is twofold and threefold, respectively. The more the anion size and charge approach the properties of the sorbed complexes, the more pronounced are the competition and effect on the sorption. In practical analyses, the concentration of anions should be minimized and held constant.

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