

## Separation of inorganic anions in acidic solution by capillary electrophoresis

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### Abstract

Inorganic anions are almost always determined by capillary electrophoresis (CE) at an alkaline pH, so the analytes will be fully ionized. However, a long-chain quaternary ammonium salt usually must be added as a flow modifier to the carrier electrolyte to reverse the direction of the electroosmotic flow. By working at a sufficiently acidic pH, the electroosmotic flow in fused-silica capillaries is virtually eliminated, and anions can be separated simply by differences in their electrophoretic mobilities. Excellent separations were obtained for  $\text{AuCl}_4^-$  and the chloro complexes of platinum group elements in HCl solution at pH 2.0 to 2.4. No additional buffer or flow modifier was needed. This CE technique is an excellent way to follow slow hydrolytic reactions in which one or more of the chloride ligands is replaced by water. Sharp peaks and good separations were also obtained for  $\text{MnO}_4^-$ ,  $\text{VO}_3^-$ , chromate, molybdate, ferrocyanide, ferricyanide and stable complex ions such as chromium oxalate ( $\text{CrOx}_3^{3-}$ ).

*Keywords:* Buffer composition; Inorganic anions

### 1. Introduction

Inorganic anions separated by capillary electrophoresis (CE) are usually analyzed by indirect photometric detection. The introduction of chromate in 1990 for the indirect detection of anions was a major advance [1]. Many excellent separations have been reported using chromate [2–6], including the separation of 30 anions in only 3 min [5]. For these separations, it was necessary to add a long-chain quaternary ammonium salt ( $\text{Q}^+$ ) as a flow modifier, to coat the capillary surface and reverse the direction of the electroosmotic flow vector.

Direct photometric detection has also been used in the CE separation of anions having sufficient absorbance in the UV or visible spectral region. Aguilar

et al. [7] separated hexacyanoferrate(II) and (III) ions at pH 7. The ionic mobilities of these highly charged ions are so large that they migrated towards the anode and against the electroosmotic flow. Buchberger et al. [8] separated twelve metal–cyanide complexes in an electrolyte containing a 20 mM phosphate buffer and 1–2 mM sodium cyanide.

In the vast majority of publications, CE separations of inorganic anions are carried out at an alkaline pH to ensure that the analytes will be in the ionic rather than the molecular form. In our research, a very acidic pH is used for the CE separation of inorganic anions. Special attention was paid to the anionic chloro complexes of gold(III) and the platinum group elements (PGEs), which are more resistant to hydrolysis in more acidic solutions. By working at lower pH values, the capillary's silanol groups are hardly ionized and, consequently, the

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electroosmotic flow is minimal. No flow modifier is therefore needed.

## 2. Experimental

### 2.1. Apparatus

CE was performed with a Waters Quanta 4000 capillary electrophoresis system (Millipore Waters, Milford, MA, USA), equipped with a negative power supply. The polyamide-coated, fused-silica capillaries used (Polymicro Technology, Phoenix, AZ, USA) were 60 cm in length with an I.D. of 75  $\mu\text{m}$ . The distance from the point of injection to the window of on-column detection was 52.25 or 52.75 cm. Direct UV detection was employed at 214 and 254 nm. A voltage of  $-10$  kV was applied for the separations. The time of hydrodynamic injection was 30 s. Electropherograms were collected and plotted by the data acquisition system Chrom Perfect Direct (Justice Innovations, Mountain View, CA, USA).

### 2.2. Procedure

New capillaries were conditioned by rinsing with 0.1 M NaOH for 1 h followed by a 1-h rinse with deionized water. At the start of each day, the capillary was rinsed with 0.1 M NaOH for 10 min, deionized water for 10 min, 0.1 M HCl for 10 min, deionized water for 10 min, and the electrolyte solution for 30 min. The capillary was also purged with the electrolyte solution for 5 min before each run.

### 2.3. Reagents

All standards and electrolytes were prepared with analytical-reagent grade chemicals and 18 M $\Omega$  deionized waters obtained from a Barnstead Nanopure II system (Sybron Barnstead, Boston, MA, USA). For the electrolyte solution, a dilute solution of reagent-grade sodium hydroxide was added to 50 ml of 0.1 M HCl, to adjust the pH to 2.4. The electrolyte solution contained 4 mM  $\text{H}^+$  (pH 2.4) and 25 mM  $\text{Cl}^-$  (Fisher Scientific, Fairlawn, NJ, USA). The potassium salts of the chloro complexes of the platinum group metals and gold and the

mercury(II) chloride were obtained from Aldrich (Milwaukee, WI, USA). The stock solutions were prepared at a concentration of 4 g/l in 40% HCl. The potassium permanganate, potassium perrhenate(VII), ammonium metavanadate, sodium chromate, sodium molybdate(VI) dihydrate, potassium chromium(III) oxalate trihydrate, potassium ferricyanide(III) and potassium ferrocyanide(II) trihydrate were also obtained from Aldrich. The stock solutions were prepared at a concentration of 4 g/l in deionized water.

## 3. Results and discussion

### 3.1. Chloro complexes of gold(III) and PGEs

In establishing conditions for CE separations, the capillary electrolyte contained chloride ions at an acidic pH to provide an environment where the chloro complex anions would be stable.

Preliminary experiments were carried out by diluting stock solutions of  $\text{AuCl}_4^-$ ,  $\text{PtCl}_6^{2-}$  and  $\text{RhCl}_6^{3-}$  with water just before analysis by CE. Spectral measurements indicated that direct detection at 254 or 214 nm would be feasible. At first, buffers prepared by adding hydrochloric acid to  $\beta$ -alanine or glycine were used at pH values ranging from about pH 3.5 to 2.5. No peak was observed for  $\text{AuCl}_4^-$  with the  $\beta$ -alanine buffer. Peaks were obtained for the sample ions in the glycine buffer, but they were broad and the baseline was noisy. Much better results were obtained when only hydrochloric acid was added to the aqueous electrolyte solution. The best results were obtained at a pH of 2.4, although the sample anion peaks were almost as sharp at pH 2.0. The electropherograms were very poor when higher HCl concentrations were used and the pH was below 1.8.

The relatively high concentration of HCl in the electrolyte solution results in a high current ( $>200$   $\mu\text{A}$  in some cases) and a noisy baseline, probably due to Joule heating. Reduction of the applied voltage from  $-20$  to  $-10$  kV greatly improved the separations. An applied voltage of  $-10$  kV was found to be the optimum. The electropherogram in Fig. 1 shows a very sharp, reproducible peak for gold(III) and a flat, smooth baseline.

Chloro complexes of PGE also gave sharp peaks

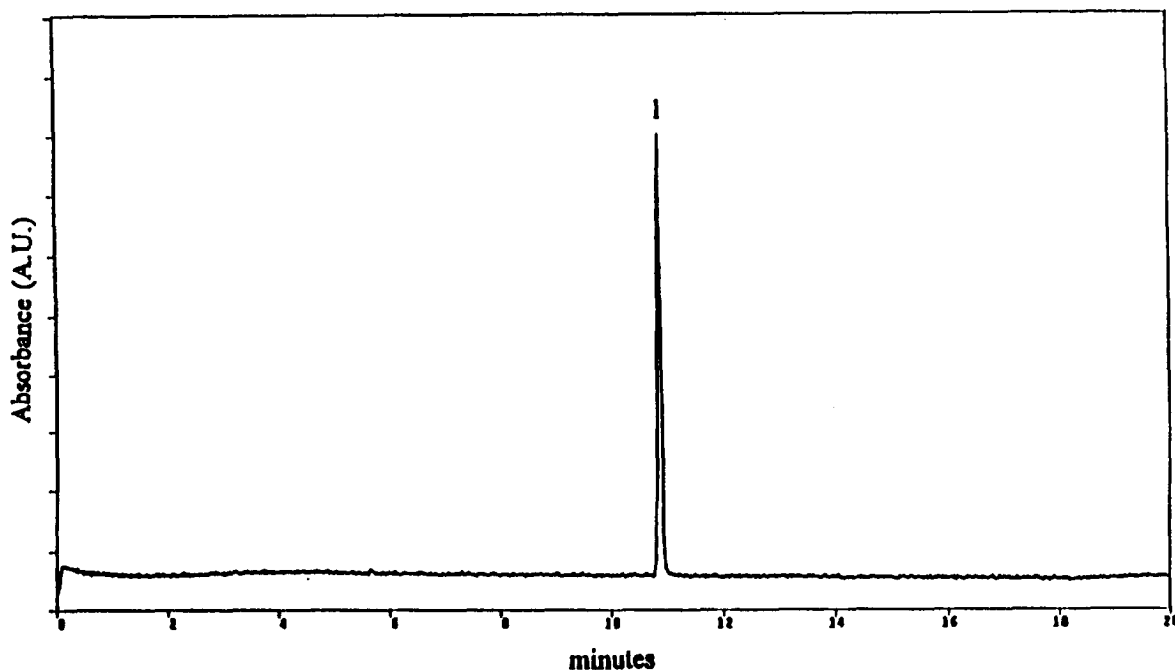


Fig. 1. Electropherogram of  $10 \mu\text{g ml}^{-1}$  of gold(III) ( $\text{AuCl}_4^-$ ). Conditions: fused-silica capillary, 60 cm (52.75 cm to detector)  $\times$  75  $\mu\text{m}$  I.D.; carrier solution, 4 mM  $\text{H}^+$ –25 mM  $\text{Cl}^-$ ; applied voltage, –10 kV; UV detection at 214 nm; sampling time, 30 s. Peak: (1)  $\text{AuCl}_4^-$ .

under the same conditions used for gold(III). A sharp single peak was obtained for  $\text{OsCl}_6^{2-}$  (7.41 min),  $\text{PdCl}_4^{2-}$  (9.30 min) and  $\text{PtCl}_4^{2-}$  (6.19 min). Palladium(IV) gave a single peak at the same time as palladium(II), indicating that the palladium(IV) had been reduced in the solution used.

Several PGE anions gave more than one peak. Platinum(IV) had a major peak at 7.5 min, a much smaller peak at 15.0 min and a contaminant peak at 6.6 min. Iridium(III) gave a peak at 6.5 min and a somewhat smaller peak at 8.7 min. The second peak in these cases is probably the result of hydrolysis in which one of the chloride atoms is replaced by water. Such hydrolysis effects are shown dramatically by rhodium(III). Fig. 2 shows a major peak for  $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$  and only a very small later peak when the stock solution (in 40% HCl) was diluted and run immediately. In Fig. 3, it can be seen that the electropherogram that was run 24 h after dilution was entirely different. The initial peak had all but disappeared while two large, late peaks had formed. The  $\text{RhCl}_6^{3-}$  had obviously undergone extensive hydrolysis. Similar behavior was observed for os-

mium(IV). After 48 h, the initial  $\text{OsCl}_6^{2-}$  peak (7.4 min) was decreased in size and a second peak at 11.2 min had appeared. The latter peak is believed to be  $\text{OsCl}_5(\text{H}_2\text{O})^-$ .

As research on chloro complex anions was being completed, publications by Baraj et al. were noted [9,10]. They were able to separate  $\text{AuCl}_4^-$ ,  $\text{PdCl}_4^{2-}$  and  $\text{PtCl}_6^{2-}$  within 18 min using an electrolyte solution containing 0.1 M HCl and 0.4 M NaCl with a low applied voltage of –7 kV. We tried the same conditions to see whether the increased acidity and higher chloride concentration would slow down the rate of hydrolysis of the complex anions. However, no noticeable improvement was observed. The main differences were a less stable baseline, poorer peak shape and longer migration times at the higher HCl and NaCl concentrations.

The average migration times for peaks of gold(III) and the PGE are given in Table 1. Reproducibility was quite good, as indicated by the statistical data given in this table. Peaks resulting from partial hydrolysis of the major peaks were assumed to contain  $\text{H}_2\text{O}$  in the coordination sphere in place of

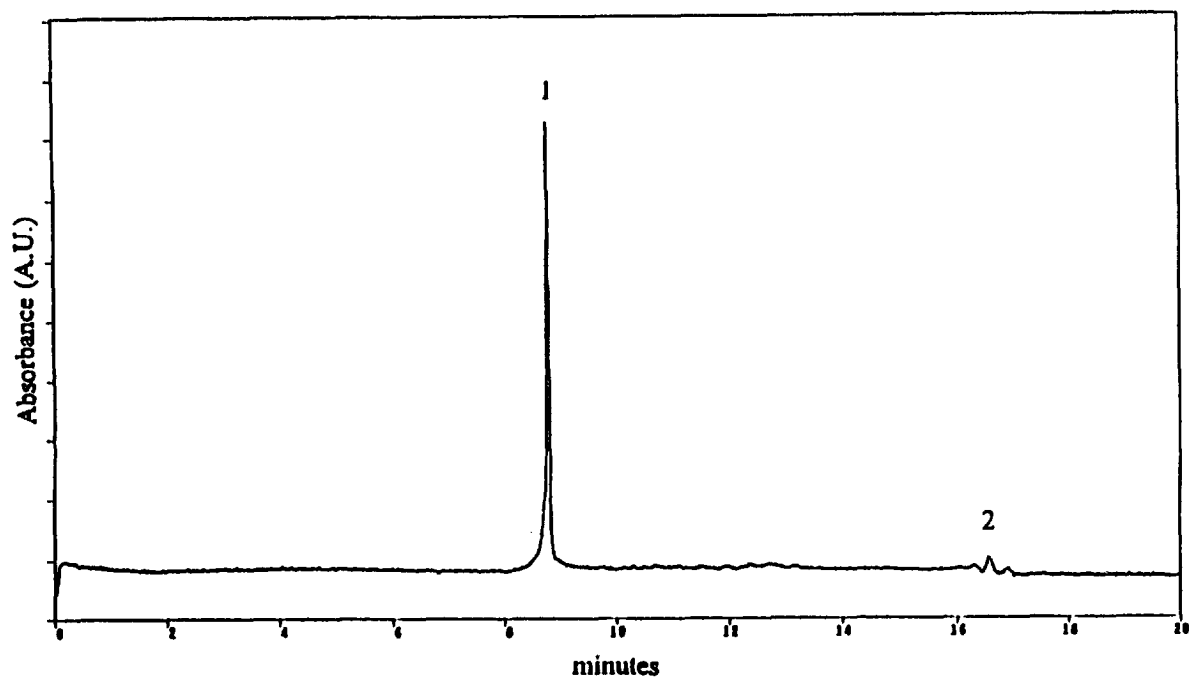


Fig. 2. Electropherogram of  $10 \mu\text{g ml}^{-1}$  of rhodium(III) ( $\text{RhCl}_6^{3-}$ ). Peaks: (1)  $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$  and (2)  $\text{RhCl}_4(\text{H}_2\text{O})_2^{--}$ . Conditions as in Fig. 1 except that the length of the capillary to the detector was 52.25 cm.

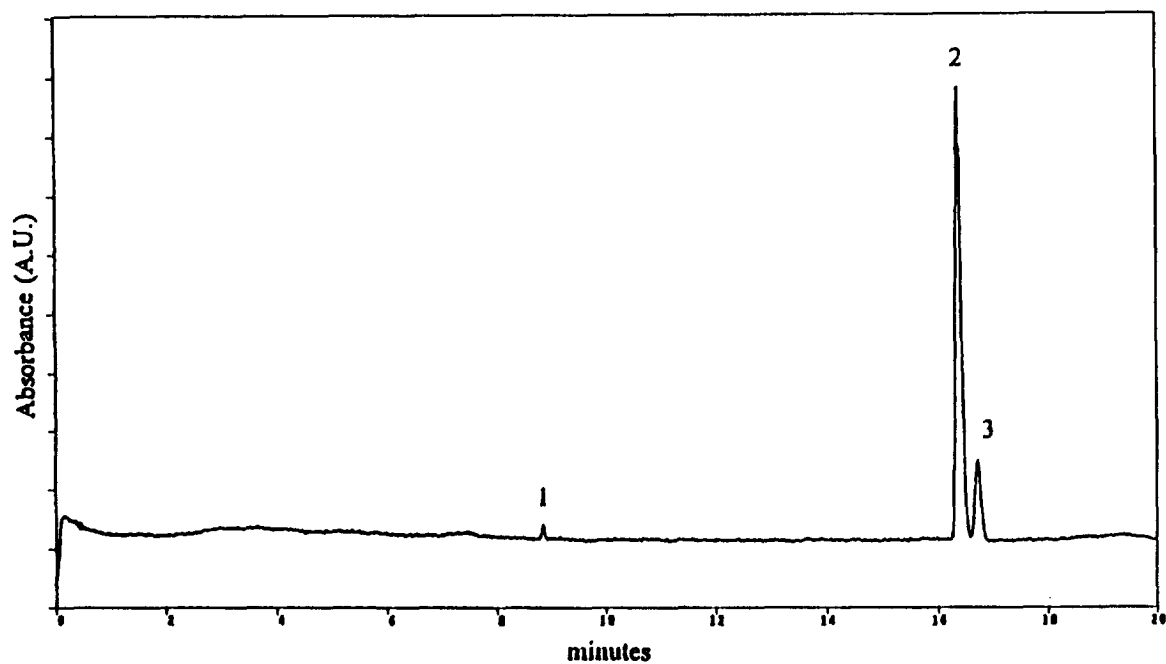


Fig. 3. Electropherogram of  $10 \mu\text{g ml}^{-1}$  of rhodium(III) ( $\text{RhCl}_6^{3-}$ ) after 24 h. Peaks: (1)  $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$ , (2)  $\text{RhCl}_4(\text{H}_2\text{O})_2^{--}$  and (3)  $\text{RhCl}_3\text{OH}(\text{H}_2\text{O})_2^-$ . Conditions as in Fig. 1.

Table 1  
Average migration times ( $t_m$ ) of the chloro complexes of the noble metals

Analyte	$t_m$ (min)	SD (min)	R.S.D. (%)	$n$
Gold(III)				
$\text{AuCl}_4^-$	10.60	0.11	1	7
Iridium(III)				
$\text{IrCl}_6^{3-}$	6.51	0.03	0.5	3
$\text{IrCl}_5(\text{H}_2\text{O})^{2-}$	8.78	0.07	0.8	3
$\text{IrCl}_4(\text{H}_2\text{O})_2^-$	16.49	0.12	0.7	3
Iridium(IV)				
$\text{IrCl}_6^{3-}$ (Ir III)	6.49	0.04	0.6	3
$\text{IrCl}_6^{2-}$	7.47	0.05	0.7	3
$\text{IrCl}_5(\text{H}_2\text{O})^{2-}$ (Ir III)	8.73	0.08	1	2
$\text{IrCl}_5(\text{H}_2\text{O})^-$	16.42	0.23	1.4	3
Osmium(IV)				
$\text{OsCl}_6^{2-}$	7.41	0.05	0.6	8
$\text{OsCl}_5(\text{H}_2\text{O})^-$	11.19	0.09	0.8	3
Palladium(II)				
$\text{PdCl}_4^{2-}$	–	0	0	6
$\text{PdCl}_3(\text{H}_2\text{O})^-$	8.91	0.02	0.2	6
Palladium(IV)				
$\text{PdCl}_6^{2-}$	–	0	0	4
$\text{PdCl}_5(\text{H}_2\text{O})^-$	9.30	0.08	0.9	4
Platinum(II)				
$\text{PtCl}_4^{2-}$	6.19	0.03	0.5	8
$\text{PtCl}_3(\text{H}_2\text{O})^-$	12.98	0.09	0.7	4
Platinum(IV)				
Contaminant	6.58	0.13	1.9	3
$\text{PtCl}_6^{2-}$	7.50	0.13	1.8	4
$\text{PtCl}_5(\text{H}_2\text{O})^-$	15.00	0.14	0.9	3
Rhodium(III)				
$\text{RhCl}_6^{3-}$	–	0	0	5
$\text{RhCl}_5(\text{H}_2\text{O})^{2-}$	8.78	0.07	0.8	5
$\text{RhCl}_4(\text{H}_2\text{O})_2^-$	16.09	0.06	0.4	3
$\text{RhCl}_3\text{OH}(\text{H}_2\text{O})^-$	16.34	0.04	0.2	3
Ruthenium(III)				
$\text{RuCl}_6^{3-}$	–	0	0	2
$\text{RuCl}_5(\text{H}_2\text{O})^{2-}$	9.51	0.01	0.1	2
$\text{RuCl}_4(\text{H}_2\text{O})_2^-$	13.51	0.01	0.1	2
$\text{RuCl}_3\text{OH}(\text{H}_2\text{O})_2^-$	16.32	0.10	0.6	5

SD is the standard deviation.

R.S.D. is the relative standard deviation.

$n$  is the number of replications.

Conditions as in Fig. 1

one or more of the chloride atoms in the parent peak, but this was not proven.

Samples containing several anionic complexes

were separated by CE to confirm the predictions that could be made from the data in Table 1. These include: Resolution of Pt(II)–(IV) mixtures (Fig. 4); separation of  $\text{IrCl}_6^{3-}$ ,  $\text{IrCl}_6^{2-}$  and  $\text{IrCl}_5(\text{H}_2\text{O})^{2-}$ ; separation of  $\text{OsCl}_6^{2-}$ ,  $\text{PdCl}_4^{2-}$ ,  $\text{AuCl}_4^-$  and  $\text{RuCl}_4(\text{H}_2\text{O})_2^-$ ; separation of eight anions (Fig. 5).

Oxidation–reduction reactions between anions of the noble metals can occur in solution. For example, the standard electrode potentials for  $\text{AuCl}_4^-$ – $\text{AuCl}_2^-$  ( $E^\circ=0.93$  V) and  $\text{PtCl}_6^{2-}$ – $\text{PtCl}_4^{2-}$  ( $E^\circ=0.68$  V) suggests that gold(III) will oxidize platinum(II) to platinum(IV).

The products of an oxidation–reduction between  $\text{AuCl}_4^-$  and  $\text{PtCl}_4^{2-}$  are shown in Fig. 6. The peaks for platinum(IV) chloro complexes appear in the electropherogram along with the peaks for the unreacted chloro complexes of the gold(III) and platinum(II). The gold(I) chloro complex ( $\text{AuCl}_2^-$ ) is probably reduced further to  $\text{Au}^0$ , so a peak is not observed for it.

Quantitative determinations are feasible. Linear calibration plots between 3 and 30 ppm were obtained for several elements that give only one peak: Pt(II),  $r=0.9997$ ; Au(III),  $r=0.998$  and Os(IV);  $r=0.997$ . However, for plots of peak height vs. concentration, the chloride concentration of samples needs to be kept constant. For  $\text{AuCl}_4^-$ , the greatest peak height occurred when the chloride concentration in the sample was 8 mM (Fig. 7). This is due to electrostacking, where the analyte zone becomes concentrated into a thin band within the capillary. The optimum concentration of 8 mM corresponds to a three to one ratio between the chloride concentration of the carrier electrolyte and that of the sample.

### 3.2. Separation of other anions

Other inorganic anions can also be separated by CE at pH 2.4 in a hydrochloric acid solution. Fig. 8 shows a good separation of  $\text{MnO}_4^-$ ,  $\text{ReO}_4^-$ ,  $\text{VO}_3^-$ , a complex chromium(III) trioxalate anion and a chromium(VI) anion. CE is attractive for the separation of strongly oxidizing ions such as permanganate and vanadate because the ions are not in contact with any organic matter that might reduce the anions. A chloro complex of mercury(II), probably  $\text{HgCl}_4^{2-}$ ,

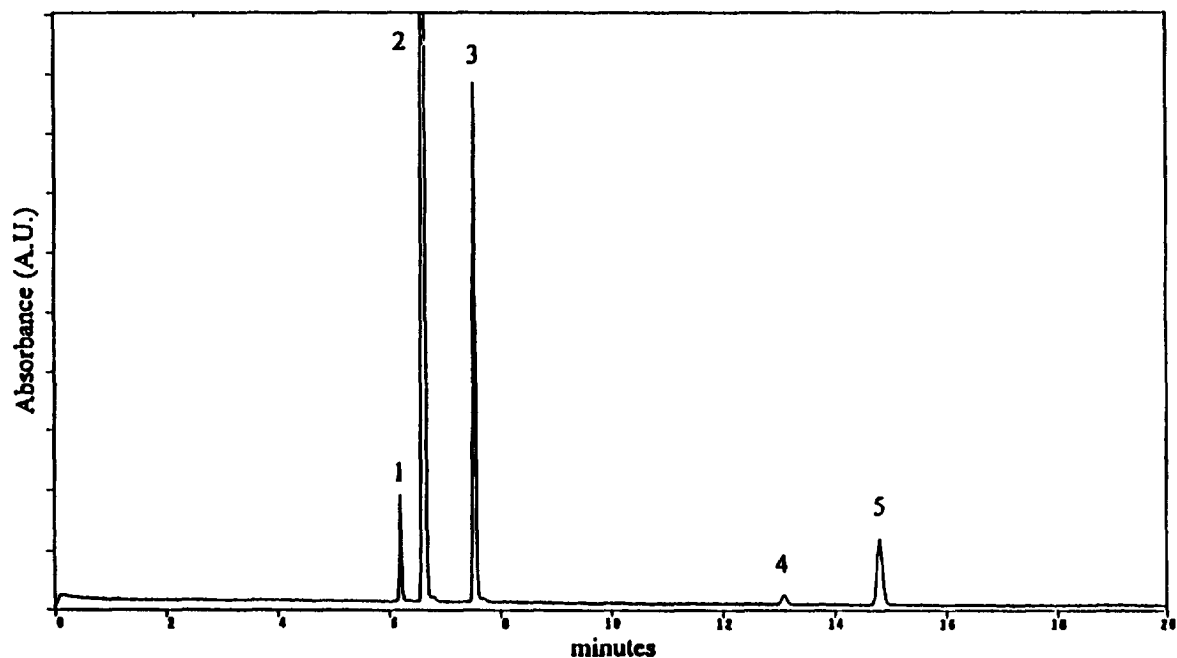


Fig. 4. Electropherogram of the chloro complexes of Pt(II) and Pt(IV) at  $20 \mu\text{g ml}^{-1}$  each. Peaks: (1)  $\text{PtCl}_4^{2-}$ , (2) contaminant, (3)  $\text{PtCl}_6^{2-}$ , (4)  $\text{PtCl}_3(\text{H}_2\text{O})^-$  and (5)  $\text{PtCl}_5(\text{H}_2\text{O})^-$ . Conditions as in Fig. 1.

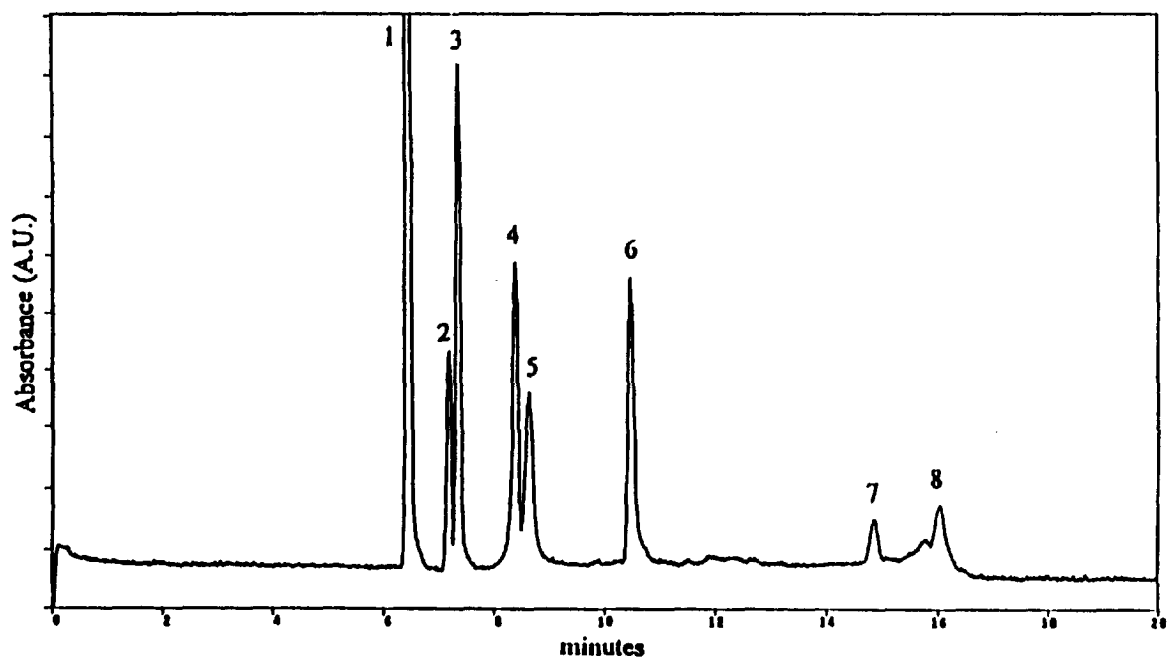


Fig. 5. Electropherogram showing the separation of the chloro complexes of osmium(IV), platinum(IV), rhodium(III), palladium(II), gold(III) and ruthenium(III) at  $10 \mu\text{g ml}^{-1}$  each. Peaks: (1) contaminant, (2) Os(IV) ( $\text{OsCl}_6^{2-}$ ), (3) Pt(IV) ( $\text{PtCl}_6^{2-}$ ), (4) Rh(III) ( $\text{RhCl}_6^{3-}$ ), (5) Pd(II) ( $\text{PdCl}_4^{2-}$ ), (6) Au(III) ( $\text{AuCl}_4^-$ ), (7) Pt(IV) [ $\text{PtCl}_5(\text{H}_2\text{O})^-$ ] and (8) Ru(III) [ $\text{RuCl}_5\text{OH}(\text{H}_2\text{O})_2^-$ ]. Conditions as in Fig. 2.

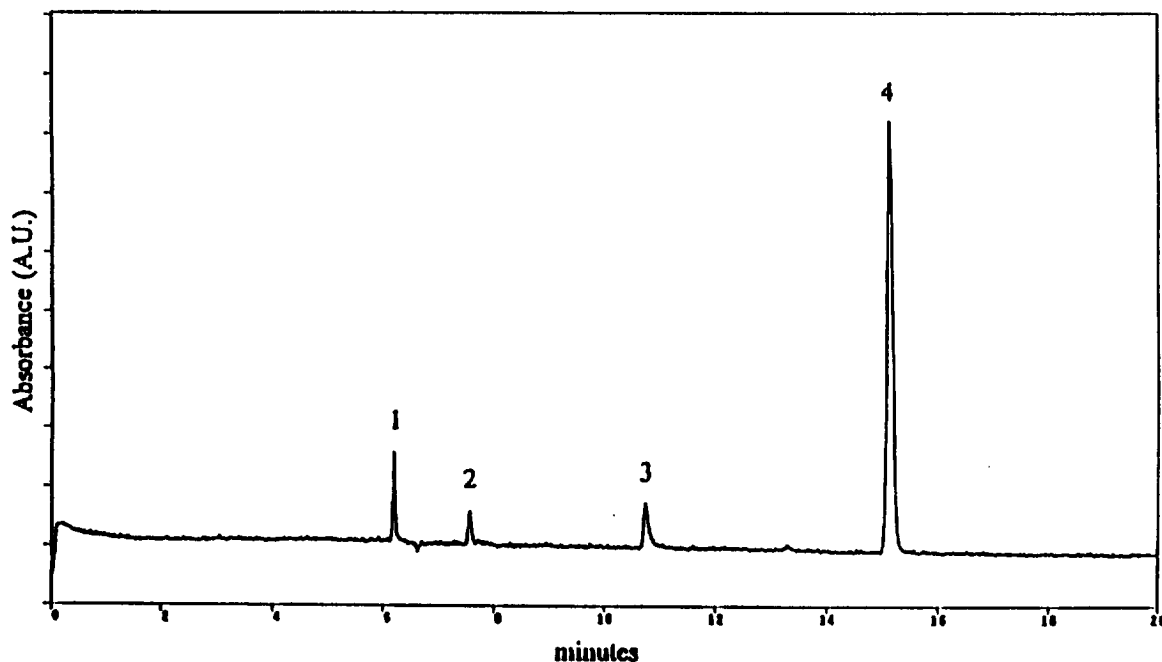


Fig. 6. Electropherogram showing the redox reaction between  $20 \mu\text{g ml}^{-1}$  of  $\text{PtCl}_4^{2-}$  and  $10 \mu\text{g ml}^{-1}$  of  $\text{AuCl}_4^-$ . Peaks: (1)  $\text{PtCl}_4^{2-}$ , (2)  $\text{PtCl}_6^{2-}$ , (3)  $\text{AuCl}_4^-$  and (4)  $\text{PtCl}_5(\text{H}_2\text{O})^-$ . Conditions as in Fig. 2.

could also be separated ( $t_m = 14.0$  min), although the peak was rather broad.

The effect of pH on the CE behavior of

chromium(VI) and molybdenum(VI) anions was studied. A symmetrical peak was obtained for chromium(VI) between pH 2.0 and 4.4. At pH 5.1,

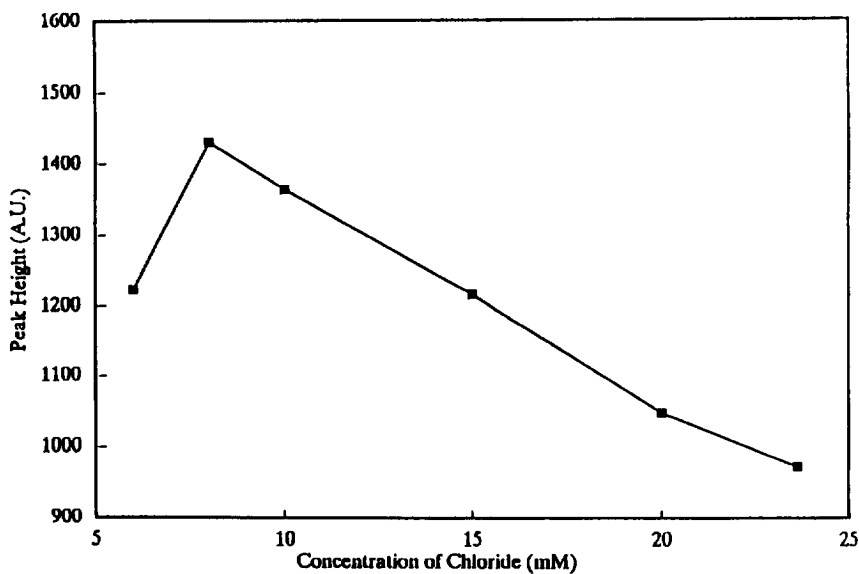


Fig. 7. Effect of chloride concentration in the sample dilution of the gold(III) chloro complex on the peak height. Conditions as in Fig. 1.

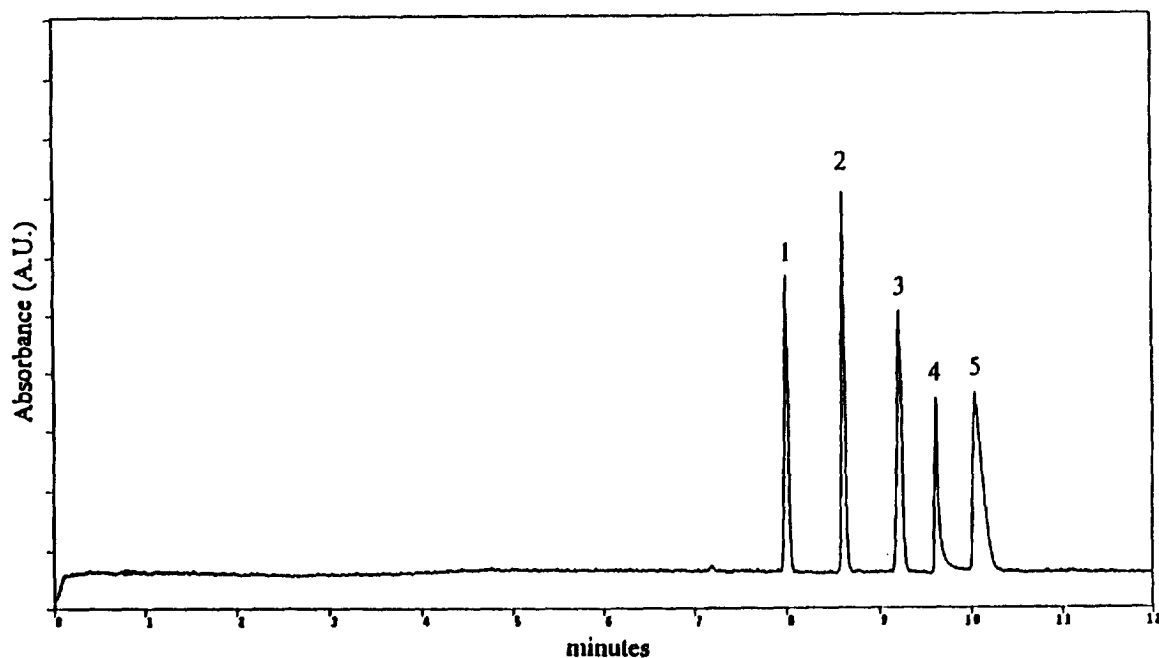


Fig. 8. Electropherogram showing the separation of the anions permanganate ( $35 \mu\text{g ml}^{-1}$ ), chromium oxalate ( $10 \mu\text{g ml}^{-1}$ ), perrhenate ( $20 \mu\text{g ml}^{-1}$ ), vanadate ( $20 \mu\text{g ml}^{-1}$ ) and chromate ( $20 \mu\text{g ml}^{-1}$ ). Peaks: (1)  $\text{MnO}_4^-$ , (2)  $\text{CrOx}_3^-$ , (3)  $\text{ReO}_4^-$ , (4)  $\text{VO}_3^-$  and (5)  $\text{Cr}_2\text{O}_7^{2-}$ . Conditions as in Fig. 2.

the peak started to broaden and tail, up to pH 6.7. Between pH 7.2 and 8.5, a sharp symmetrical peak was obtained. The acid dissociation constants for  $\text{H}_2\text{CrO}_4$  have been given as  $k_1 = 1 \cdot 10^{0.2}$  and  $k_2 = 1 \cdot 10^{-6.5}$  [11]. Thus, the peak observed between pH 2.0 and 4.4 is most likely  $\text{HCrO}_4^-$  or the dimer,  $\text{Cr}_2\text{O}_7^{2-}$ . The peak observed between pH 7.2 and 8.5 would be  $\text{CrO}_4^{2-}$ .

Acid dissociation constants for  $\text{H}_2\text{MoO}_4$  have been given as  $k_1 = 1 \cdot 10^{-4.0}$  and  $k_2 = 1 \cdot 10^{-4.24}$  [11]. No peak was detected for molybdenum(VI) until pH 3.8 and a sharp symmetrical peak was not obtained until pH 6.6. This was probably  $\text{MoO}_4^{2-}$ .

Sharp peaks were obtained for both ferrocyanide [ $\text{Fe}(\text{CN})_6^{4-}$ ,  $t_m = 8.3$  min] and ferricyanide [ $\text{Fe}(\text{CN})_6^{3-}$ ,  $t_m = 6.5$  min]. From the formulas above, ferrocyanide with a negative four charge would be expected to migrate faster than ferricyanide with a negative three charge. However, the acid dissociation constants need to be considered: For  $\text{H}_2\text{Fe}(\text{CN})_6^{2-}$ ,  $k_1 = 1 \cdot 10^{-1.9}$  and  $k_2 = 1 \cdot 10^{-3.7}$  [11]. At pH 2.4, the average charge was calculated to be 2.8, which is

less than 3, for ferricyanide for which no acid dissociation constants were listed.

Sharp peaks were obtained for several additional inorganic anions in HCl solution at pH 2.4:  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{SCN}^-$ ,  $\text{IO}_4^-$ , and  $\text{IO}_3^-$ . Migration times for the inorganic anions studied (other than the noble metals) are given in Table 2. The migration times were very reproducible, with a relative standard deviation of 0.6%.

The use of electrolytes containing perchloric acid instead of hydrochloric acid was investigated briefly. A separation of five anions in perchloric acid at pH 2.4 is shown in Fig. 9. The migration times were similar to those obtained in hydrochloric acid at the same pH. Electropherograms for the same ions (see Fig. 9) were also run in more acidic solutions of perchloric acid. Good separations were obtained in perchloric acid at pH 2.0 and 1.8, but an attempted separation at pH 1.6 gave a very erratic baseline with no good peaks for the anionic analytes.

The effect of pH was studied over a broad range for several anions. Observed mobilities are plotted as



Table 2  
Average migration times ( $t_m$ ) of other metal anions

Analyte	$t_m$ (min)	SD (min)	R.S.D. (%)	$n$
$\text{Cr}_2\text{O}_7^{2-}$	10.06	0.03	0.3	3
$\text{CrO}_4^{2-}$	8.62	0.04	0.5	3
$\text{HgCl}_4^{2-}$	13.95	0.06	0.4	2
$\text{MnO}_4^-$	8.06	0.08	1	2
$\text{ReO}_4^-$	9.23	0.03	0.3	3
$\text{VO}_3^-$	9.61	0.02	0.2	3
$\text{MoO}_4^{2-}$	12.44	0.00	0	1
$\text{Fe}(\text{CN})_6^{3-}$	6.53	0.09	1.4	3
$\text{HFe}(\text{CN})_6^{3-}$	8.33	0.03	0.3	3
$\text{I}^-$	5.68	0.01	0.20	3
$\text{NO}_3^-$	6.26	0.01	0.12	6
$\text{SCN}^-$	6.61	0.01	0.12	6
$\text{IO}_4^-$	8.61	0.01	0.18	3
$\text{IO}_3^-$	10.95	0.04	0.36	6
$\text{Br}^-$	5.63	0.01	0.10	3

SD is the standard deviation.

R.S.D. is the relative standard deviation

$n$  is the number of replications.

Conditions as in Fig. 2 except for molybdate at pH 6.6.

a function of pH in Fig. 10. The rapid drop in mobility just above pH 5 is due to an increased electroosmotic mobility as the capillary's silanol

groups became more ionized. The electroosmotic mobility, which was measured by reversing the direction of the applied voltage, jumped from 0.13 ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ) at pH 5.0 to 0.40 at pH 5.2 and then increased gradually to 0.46 at pH 8.0. The electroosmotic mobility at pH 4.0 was 0.08 and was too low to be measured at even more acidic pH values. Electrophoretic mobilities remained almost constant between pH 4 and 8. These data show that anions can be separated by CE between pH values of 1.8 and 5.0.

#### 4. Conclusions

Anionic chloro complexes of the noble metals, as well as a number of other inorganic anions, can be separated efficiently in very acidic solutions (pH 2.4) by capillary electrophoresis. Although the currents were higher than normally encountered in CE, sharp peaks and stable baselines were obtained by operating at a relatively low applied voltage ( $-10 \text{ kV}$ ). The method used was the utmost in simplicity for

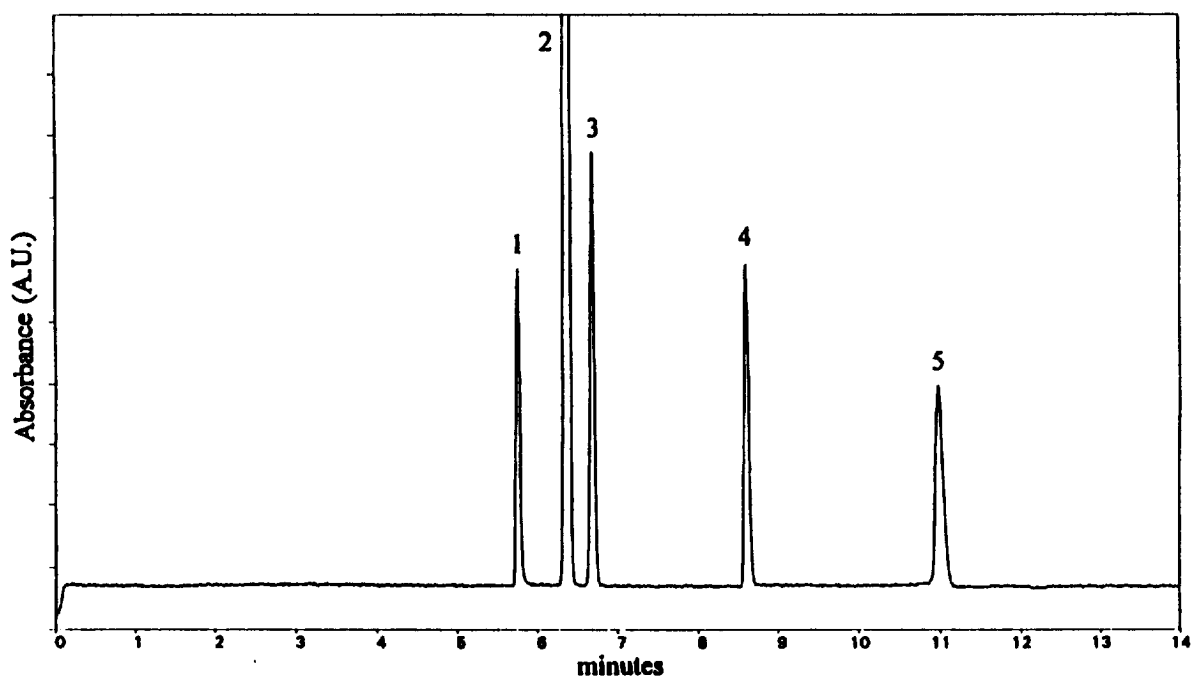


Fig. 9. Separation of inorganic anions in 25 mM perchloric acid (pH 2.4). Other conditions as in Fig. 2. Peaks: (1)  $\text{I}^-$ , (2)  $\text{NO}_3^-$ , (3)  $\text{SCN}^-$ , (4)  $\text{IO}_4^-$  and (5)  $\text{IO}_3^-$ .

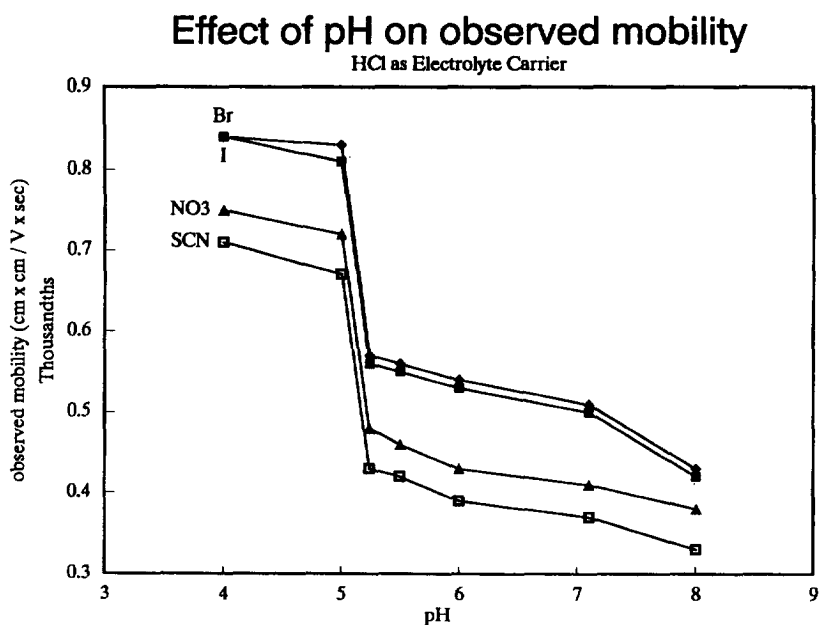


Fig. 10. Effect of pH on observed mobility. Acetate–acetic acid, ammonium acetate or ammonium acetate–sodium acetate buffers were used. Other conditions as in Fig. 2.

anions amenable to direct photometric detection. At the acidic pH values used, no buffer was needed other than HCl or HClO<sub>4</sub>. No flow modifier was required because electroosmotic flow was minimal in the acidic electrolytes that were used. This avoids the possibility of anion precipitation by positively charged flow modifiers and also avoids the surface build-up that sometimes occurs with such modifiers.

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