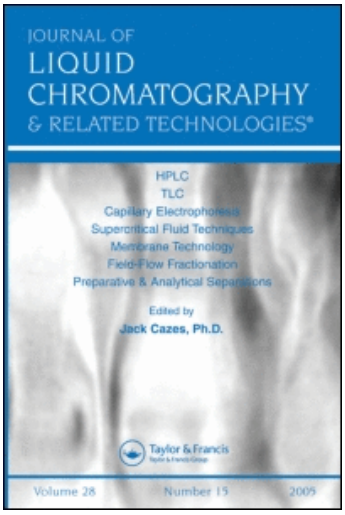

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THE SEPARATION AND INDIRECT VISIBLE DETECTION OF RARE EARTH METAL CATIONS ON A DYE-COATED STATIONARY PHASE

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ABSTRACT

The separation and indirect visible detection of rare earth metal cations on a dye-coated stationary phase was studied. Phenol Red, which is typically used for pH titrations, was used as an ion-interaction reagent in this study and is composed of a hydrophobic group and a fixed charge site. The mobile phase variables that were found to affect metal cation retention and resolution are: concentration of dye, concentration of organic modifier, mobile-phase pH, type and concentration of ligand, and ionic strength. A polymer-based stationary phase was used in this study and detection of the metal cations was accomplished by indirect visible detection at 490 nm.

INTRODUCTION

The separation of the lanthanide metals by reversed-phase chromatography has been studied using several different techniques, including ion chromatography [1], ion-interaction chromatography [2-4], ion exchange chromatography [5], micelle exclusion chromatography [6] and as an anionic complex using ion interaction chromatography [7].

Ion-interaction chromatography has been successfully employed to describe the interactions that take place between an analyte ion and a mobile-phase counterion [8-19]. A hydrophobic ion (ion-interaction reagent) that contains a fixed charge site is added to the mobile phase. The ion-interaction reagent (IIR) is sorbed onto the stationary and a charged double layer is formed. The primary layer is composed of the sorbed hydrophobic counterion while the co-ion occupies the diffuse secondary layer. The analyte ions of interest are then separated in the diffuse secondary layer, based on selectivity differences between ions.

Several recent publications have reported on the separation of inorganic and organic ions with mobile phases that contain a dye. The dyes that were studied are commonly used for pH titrations. Aliphatic acids have been separated using a Brilliant Green coated stationary phase [20], while Methylene Blue was used to separate organic and inorganic anions [21]. Inorganic anions were separated on a Methyl Green-coated column [22], while the separation of metal ions was studied with several different dyes [23]. Ethyl Violet has been successfully used in the separation and indirect visible detection of inorganic and organic anions [24]. Both polymer and silica based stationary phases were studied using Ethyl Violet mobile phases. Additionally, several metal cations have been separated using Thymol Blue as an IIR and detected using indirect visible detection [25].

In the present study, the hydrophobic dye is used as both the IIR for separating the rare earth metal cations and for their indirect visible detection. This paper describes the mobile-phase variables that affect the separation of rare earth metal cations on a dye-coated stationary phase. The results obtained are discussed.

EXPERIMENTAL

Chemicals

HPLC-grade acetonitrile was obtained from Baxter Scientific Products (McGaw Park, IL, U.S.A.). HPLC-grade water was obtained by passing de-ionized water through a Nanopure water purification unit. Phenol Red, citric acid, tartaric acid, inorganic salts, α-hydroxy isobutyric acid, and rare earth metal salts were obtained from The

Aldrich Chemical Company (Milwaukee, WI, U.S.A.). All chemicals were of reagent grade.

Apparatus

The instrumentation used in this study consisted of a Hewlett-Packard liquid chromatography system, Model 1090. The columns used were: a 4.1 x 150-mm Hamilton PRP-1 column, available from Hamilton Company (Reno, NV, U.S.A.), and a 4.6 x 150-mm PLRP-S column, available from Polymer Laboratories (Amherst, MA, U.S.A.). The PRP-1 column is a spherical, 10-μm poly(styrenedivinylbenzene) copolymeric packing. The PLRP-S column is composed of a spherical, 5-μm poly(styrenedivinylbenzene) copolymeric packing. Flow-rates of 1.0 ml/min were used. Aqueous analyte samples of about 500 μg/mL and sample aliquots of 50 μl were used. Inlet pressures of 500-2000 psi were observed. A wavelength of 490 was used for the indirect visible detection.

Mobile-Phase Preparation

The Phenol Red dye was quantitatively transferred (appropriate volume of a 0.01 M Phenol Red solution) to a beaker that contained the aqueous buffer solution. The desired pH was achieved by adding base. The aqueous solution was diluted to the appropriate volume and the organic modifier was then added. The solution was mixed and then filtered through a 0.45-μm PTFE membrane.

Column loading

Column loading was determined by running the mobile phase through the column and UV/visible detector until the breakthrough occurred. The number of μmoles of dye adsorbed on the stationary phase was calculated from the breakthrough volume [7]. The column was then allowed to equilibrate for an additional 30-60 min.

RESULTS AND DISCUSSION

The retention of inorganic and organic analyte ions on reversed stationary phases with mobile phases that contain a hydrophobic ion of opposite charge (Ion-Interaction Reagent) can be described by two major equilibria [7,8,12-15]. The first equilibrium that takes place is the sorption of the hydrophobic counterion onto the stationary phase (Eqn. 1) while the second equilibrium can be described by the interactions that take place in the diffuse secondary layer between the analyte ion and the co-ion that is associated with the retained hydrophobic ion (Eqn. 2). These equilibria are shown by Eqns. 1 and 2, respectively.

$$A + PR^- + C^- + M^+ \rightleftharpoons A^{\cdots}PR^-{}^+M + C^- \quad (1)$$

$$A^{\cdots}PR^-{}^+M + X^+ + C^- \rightleftharpoons A^{\cdots}PR^-{}^+X + C^- + M^+ \quad (2)$$

A represents the stationary phase, PR^- represents an ion-interaction reagent (UV/visible-active counteranion) in the mobile phase, M^+ is the countercation associated with the ion-interaction reagent (IIR), the buffer and/or added inert electrolyte, C^- is an anion associated with the countercation and/or the analyte cation, and X^+ is the analyte cation. The variables that have been found to affect the separation of cations are: the reversed stationary phase, the type and concentration of the IIR, the concentration of organic modifier, the type and concentration of countercation and/or buffer in the mobile phase, and the mobile-phase pH. The rare earth metal cations were found to have little or no retention on the polymer stationary phases in the absence of the IIR.

The IIR (Phenol Red) contains a chromophoric group which will allow the analyte cations to be detected indirectly. The absorbance of the UV/visible detector must be kept below 0.8 A.U.F.S. when using indirect visible detection. If the absorbance exceeds 0.8 A.U.F.S., the detector may be outside of the linear working range. The detection of analyte cations by indirect visible detection can be explained by differences in the relative concentrations of the IIR in the effluent. As an analyte cation travels down the column (Eqns. 1 and 2), the concentration of the UV-absorbing IIR band changes relative to the

background absorbance. A positive chromatographic peak is observed when the concentration of the IIR in the analyte band increases, due to its removal from the column, or a negative chromatographic peak is observed if the concentration of the IIR decreases, due to its uptake onto the stationary phase. The mobile phase added IIR is responsible for both the retention of the analyte cations and in their indirect visible detection.

In order for the metal cations to have reasonable retention times, a ligand was added to the mobile phase. The differences in complexation between the metal cation and the ligand will lead to differences in cation retention, selectivity and resolution. The stronger the complexation between the ligand and the metal cation, the faster the cation will elute off the column.

Effect of Phenol Red Concentration

The first mobile phase parameter studied was the mobile phase concentration of Phenol Red and what effect that would have on analyte cation retention. As the mobile phase concentration of Phenol Red was increased, a corresponding increase in the amount of Phenol Red adsorbed onto the stationary phase was observed (Figure 1). The increased adsorption of Phenol Red leads to an increase in the number of apparent cation exchange sites. The number of cation exchange sites found for the Phenol Red was similar to that of low-capacity fixed-site cation exchangers [16-18,25] and to mobile phases that contain ion-interaction reagents, such as alkylsulfonate salts [1-18].

As the amount of Phenol Red that is adsorbed onto the stationary phase increases, the number of cation exchange sites increases (Figure 1) which should lead to higher analyte cation retention. The retention times of several metal cations at different mobile phase concentrations of Phenol Red is shown in Figure 2. Although the higher concentration of Phenol Red provided higher retention times for the cations, the lower concentration of Phenol Red (0.1 mM) provided a better separation and better sensitivity. Mobile phase Phenol Red concentrations above 0.15 mM had absorbances well above 0.8 A.U.F.S.

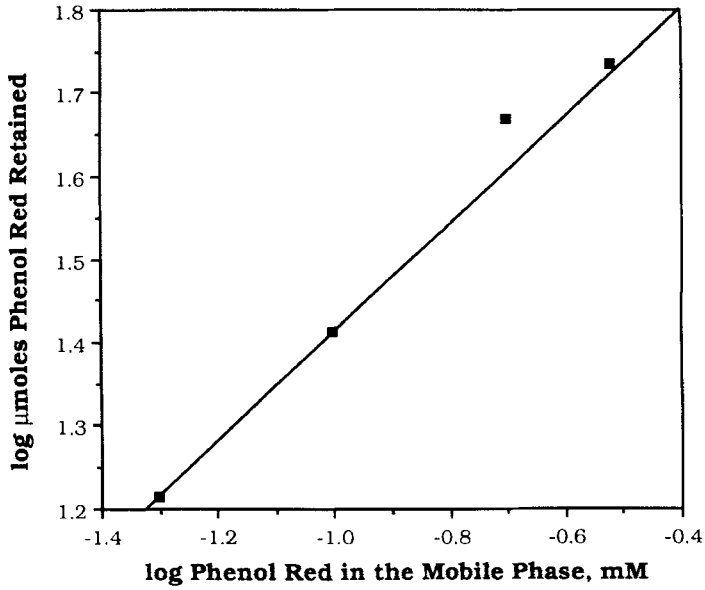

Figure 1. Amount of Phenol Red adsorbed on the PLRP-S stationary phase as a function of the mobile phase concentration of Phenol Red. Mobile phase: Phenol Red, 20.0 mM α-hydroxyisobutyric acid (pH 3.7), 2% CH_3CN/98% H_2O.

and were found to be outside of the linear working range of the detector.

Mobile-Phase Variables: Effect on Phenol Red Adsorption

As the concentration of organic modifier present in the mobile phase was increased the amount of Phenol Red adsorbed on the stationary phase was found to decrease (Table I). This, in turn, leads to a decrease in the number of cation exchange sites present on the stationary phase and a corresponding decrease in analyte cation *retention.*

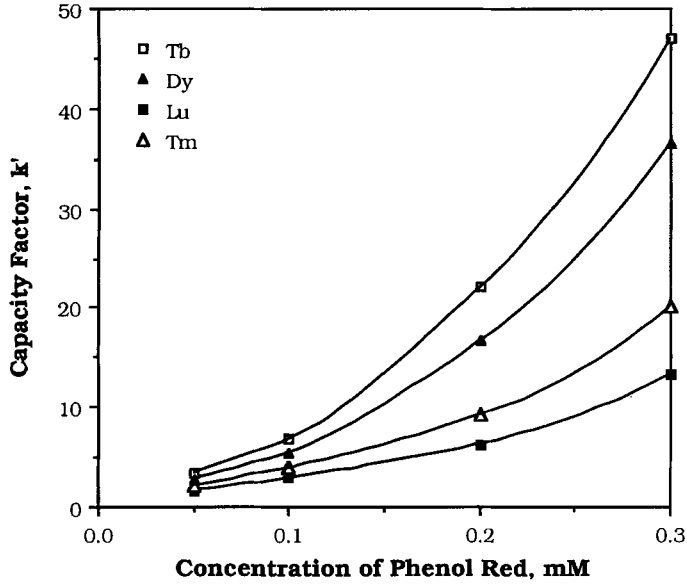

Figure 2. The effect that the mobile phase concentration of Phenol Red had on analyte cation retention. Mobile phase: Phenol Red, 20.0 mM α-hydroxyisobutyric acid (pH 3.7), 2% CH_3CN/98% H_2O.

TABLE I

Amount of Phenol Red Adsorbed on PLRP-S Stationary Phase versus Mobile Phase Concentration of Acetonitrile

Percent Acetonitrile	μmoles of Phenol Red Adsorbed
1.0	43.0
2.0	26.2
3.0	19.7
5.0	13.6
7.5	10.9
10.0	7.0

Mobile Phase: 0.10 mM Phenol Red, 20.0 mM α-Hydroxyisobutyric acid, pH 3.7, CH_3CN/H_2O.

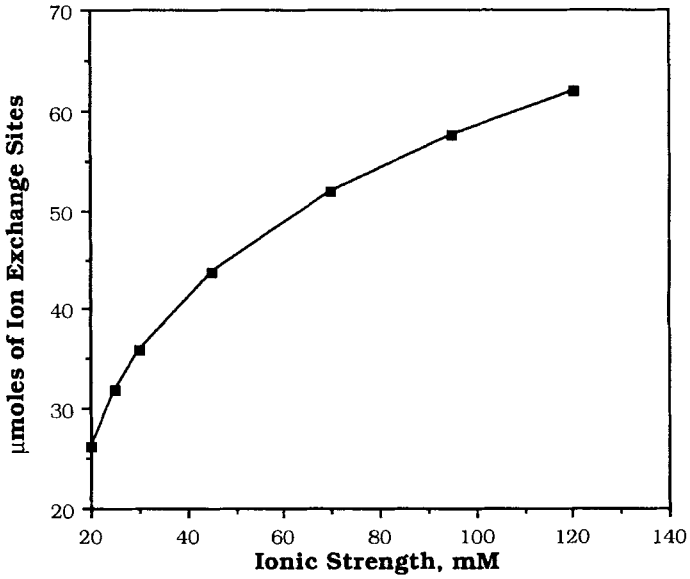

Figure 3. The number of apparent cation exchange sites on the PLRP-S stationary phase as a function of mobile phase ionic strength. Mobile phase: 0.1 mM Phenol Red, 20.0 mM α-hydroxyisobutyric acid (pH 3.7), NaCl, 2% CH_3CN/98% H_2O.

The ionic strength of the mobile phase will also affect the amount of Phenol Red adsorbed onto the stationary phase [11,16,17,19]. As the mobile-phase ionic strength was increased (addition of NaCl), a corresponding increase in the amount of Phenol Red adsorbed on the stationary phase was observed which in turn leads to an increase in the apparent number of cation-exchange sites present (Figure 5). The amount of adsorbed Phenol Red increased until an ionic strength of about 0.120 (0.075 mM NaCl) was reached, where the number of cation-exchange sites leveled off. Even though a greater number of cation-exchange sites are present at higher mobile-phase ionic strengths, increased competition for the cation-exchange sites from the higher concentration of countercations leads to decreased cation retention (see Eqn. 2).

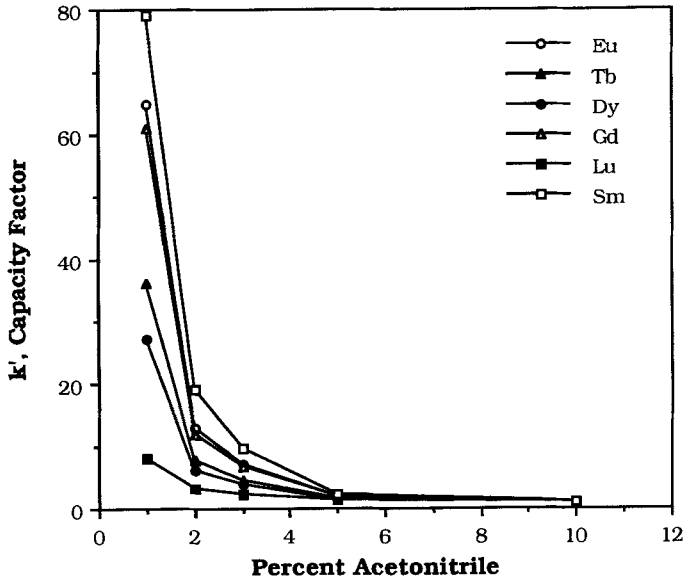

Figure 4. Effect of acetonitrile concentration on analyte cation retention. Mobile phase: 0.1 mM Phenol Red, 20.0 mM α–hydroxyisobutyric acid (pH 3.7) in CH_3CN/H_2O.

Effect of Organic Modifier on Cation Retention

Retention of the cations were found to be dependent on the number of available cation exchange sites present on the column. As mentioned previously, the adsorption of Phenol Red onto the stationary phase was found to decrease with increasing organic modifier concentration. Therefore the number of apparent cation exchange sites decreased which leads to lower cation retention. This is illustrated in Figure 4. Resolution of the analyte cations was better at the lower concentrations of acetonitrile where more cation-exchange sites were present on the stationary phase.

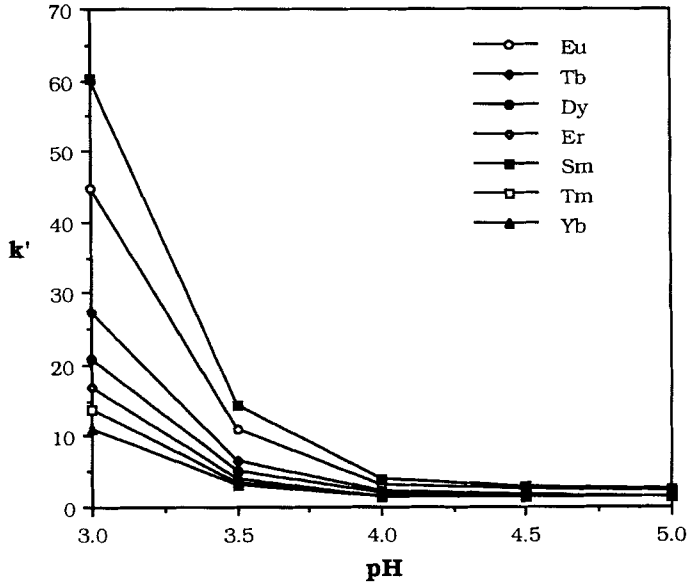

Figure 5. Effect of mobile phase pH on analyte cation retention. Mobile-phase: 0.1 mM Phenol Red, 20.0 mM α-hydroxyisobutyric acid, 2% CH_3CN/98% H_2O.

Effect of pH

The complexation between the ligand in the mobile phase and the analyte cations are affected by mobile phase pH, which in turn affects cation retention and resolution. The effect that mobile phase pH had on metal retention is shown in Figure 5. Retention times changed dramatically over the pH range of 3.0 to 4.5 (ionic strength held constant). As the pH of the mobile phase was increased, a corresponding decrease in rare earth metal retention was observed. This is attributed to the stronger complexation taking place between the ligand and the metal cation. Optimal conditions for rare earth cation retention and resolution were found to be between pH 3.5 and 4.0.

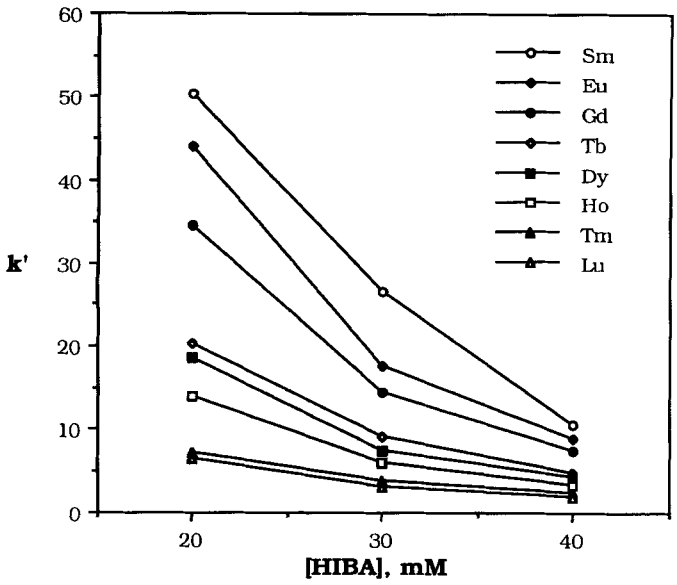

Figure 6 Effect of ligand concentration on cation retention. Mobile Phase: 0.1 mM Phenol Red, α–hydroxyisobutyric acid (pH 3.7), 2% CH_3CN/98% H_2O.

Effect of ligand concentration

The concentration of ligand in the mobile phase plays a key role in the separation of the metal cations. The complexation that takes place between the metal cation and the mobile phase ligand, as well as the amount of adsorbed IIR, will control retention and resolution. If a ligand were not added to the mobile phase, the metals would be highly retained due to the ionic interactions with the sorbed Phenol Red. If Phenol Red were absent but the mobile phase ligand was present, the metal cations would have no retention.

The results observed for the Phenol Red/α–hydroxyisobutyric acid (HIBA) mobile phases and the metal cations indicated that the ligand concentration had an effect on metal retention (Figure 6). At low concentrations of ligand, retention of the metals was very high. As the concentration of ligand was increased, metal retention decreased.

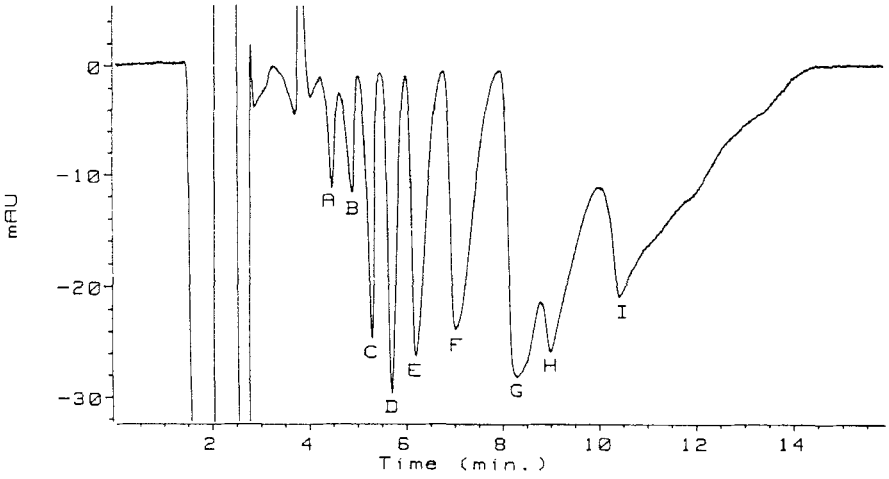

Figure 7. Separation of rare earth metals on a PLRP-S column. Mobile-phase conditions: 0.1 mM Phenol Red, 30.0 mM α–hydroxyisobutyric acid (pH 3.7), 2% CH_3CN/98% H_2O. Rare Earth Metals: A) Ce, B) Lu, C) Yb, D) Tm, E) Er, Ho, F) Dy, G) Tb, Gd, H) Eu, I) Sm.

Elution orders were found to remain the same over the ligand concentration range and were found to be: Ce < Lu < Yb < Tm < Er ≤ Ho < Dy < Tb ≤ Gd < Eu < Sm. Citrate and tartrate were also used as mobile phase added ligands, however very little differences in selectivities was observed and resolution was poor.

Effect of Ionic Strength

Sodium chloride was added to the mobile phase in order to determine the effect of ionic strength on cation retention. Retention of the cations decreased as the concentration of sodium chloride was increased. This is attributed to increased competition for the cation-exchange sites (Eqn. 2). Even though the amount of Phenol Red

adsorbed on the stationary phase increased with increasing ionic strength, metal cation retention decreased due to increased competition for the cation exchange site from the higher concentration of competing cations present.

Separation of Rare Earth Metals

The separation of the rare earth metal cations is shown in Figure 7. The mobile phase consisted of 0.1 mM Phenol Red, 30.0 mM α-HIBA (pH 3.7), 2% CH_3CN/98% H_2O using indirect visible detection at 490 nm. The flow rate was 1.0 ml/min and a 5 μm, 4.6 x 150 mm PLRP-S stationary phase was used.

Quantitation

Calibration curves were done on several of the rare earth metals. Correlation coefficients of 0.999 or better were found for a the rare earth metals that covered a cocentration range of 50 ppm to 1200 ppm. Detection limits of 25 ppm at a signal to noise ratio of 3:1 were typically found and limits of quantitation were found to be between 25 and 50 ppm.

CONCLUSIONS

A Phenol Red-coated stationary phase provided acceptable separations of the rare earth metal cations studied. The mobile-phase variables that had an affect on rare earth metal cation retention were identified and studied. The retention and separation of the rare earth metal cations can be manipulated by changing the different mobile phase parameters. Quantitation of several of the rare earth metals can easily be done using a dye coated stationary phase and indirect visible detection.

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