Spectrophotometric Determination of Gold after Separation and Preconcentration with a Solid-Phase Extraction Method

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A simple, sensitive, and inexpensive method for separation and preconcentration of gold ions from aqueous solutions prior to its spectrophotometric determination is reported. The proposed method includes two procedures. In the first one, sodium 8-aminoquinoline-5-azobenzene-4′-sulfonate (SPAQ) was immobilized directly on an alumina column which adsorbed gold ions from aqueous solutions. Then, $\mathrm{Au^{III}}$ was desorbed by HCl solution, and the absorbance of the alkaline solution in the presence of a cationic surfactant, cetyltrimethylammonium bromide (CTMAB), was measured at 611 nm. In the second procedure, Au–SPAQ complex in the presence of CTMAB in alkaline media was passed through the column containing alumina (washed with nitric acid and neutralized by washing with distilled water). The complex was then desorbed with ethanol, and the absorbance was measured immediately at 611 nm. The proposed methods were applied successfully to the determination of gold in Azerbaijan ores. The relative standard deviations for five replicate determinations of $0.2\,\mu\mathrm{g\,mL^{-1}}$ $\mathrm{Au^{III}}$ for the first and second procedures were 3.01% and 2.66%, and the corresponding limits of detection were 1.37 and $3.70\,\mu\mathrm{g\,L^{-1}}$, respectively.

Due to wide industrial applications as well as its role in economic activities, gold is one of the most important noble metals. Regardless of the type of detection method, separation and preconcentration of gold ions prior to its determination is an essential step. Even with the high sensitivity and selectivity of modern instrumental methods, such as atomic absorption spectrometry (AAS), X-ray fluorescence (XRF), inductively coupled plasma-mass spectrometry (ICP-MS), and neutron activation analysis (NAA), preconcentration and separation steps are often necessary because of the complex compositions of the real samples and trace or ultra trace concentrations of gold.[1–4]

The separation and preconcentration processes of gold ions from different matrices are mainly based on the utilization and application of available techniques including membrane disks,[5] liquid–liquid extraction,[6,7] ion-exchange and sorption,[1,8] fire assay and co-precipitation,[9] activated carbon,[10] HPLC[11] and CE,[12] and solid-phase extraction (SPE).

Since methods commonly used for determination of gold are generally complex and expensive, solid-phase extraction (SPE) technique has increasingly become popular because of several major advantages such as simple to operate, high preconcentration factor, rapid phase separation, and the ability to combine with different detection techniques. Combining solid-phase extraction (SPE) with spectrophotometry as a simple and inexpensive detection method makes it possible to introduce a simple and sensitive method for preconcentration and determination of gold in geological samples.

Among the various adsorbents used in SPE methods, alumina has been extensively studied for the adsorption of metal ions. Alumina has many desirable ion-exchange properties. It undergoes little swelling or shrinking in electrolyte solution, has good resistance towards strong oxidizing and reducing agents, and can act both as an anion or a cation exchanger depending upon solution pH.[13] Immobilizing adsorbing reagents on aluminum oxide or alumina as an inexpensive and accessible material is a suitable process for preconcentration of metal ions. In our previous works, dithizone (1,5-diphenylthiocarbazone) and 1-(2-pyridylazo)-2-naphthol were immobilized on surfactant-coated alumina for successful preconcentration of $\mathrm{Cu^{2+}}$,[14] $\mathrm{Hg^{2+}}$,[15] and $\mathrm{Co^{2+}}$.[16] We have also reported the utilization of surfactant-coated alumina for preconcentration of $\mathrm{Cr^{VI}}$–diphenylcarbazide complex[17] and chromium speciation.[18] Other alumina-based SPE methods, have been applied for separation and preconcentration of silver,[19] chromium(VI),[20] lead,[21] uranium,[22] mercury,[23] and some other metal ions.[24] In these reports, a suitable ligand was immobilized on the surfactant-coated alumina prior to the adsorption of metal ions. Such systems could also be applied for determination of organic materials.[25,26] Alumina may also directly be used for separation and preconcentration of metal ions without using any surfactant.[27,28]

In spectrophotometric determination of gold with most of the chromogenic agent, as the sensitivity is very poor, evaporation or extraction with an organic solvent for concentration is necessary. Sodium 8-aminoquinoline-5-azobenzene-4′-sulfonate (SPAQ), a derivative of 8-aminoqunoline, was synthesized for spectrophotometric determination of gold in ores and slimes, and found to be more sensitive and selective compared with other chromogenic agents.[29] Later, SPAQ was used for spectrophotometric determination of gold in a flow injection (FI) system.[30] This ligand recently has been used for copper determination in water and mineral samples.[31]

The aim of this work was to study the utilization of SPAQ immobilization on alumina for separation and preconcentration of gold from ore sample solutions. Au–SPAQ complex was also studied. The spectrophotometry coupled with the advantages of SPE methods implied a simple and sensitive method to determine gold in part per billion (ppb) levels.

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Experimental

Apparatus. A Shimadzu UV-265-FW type UV–vis spectrophotometer was used for acquiring the spectra, a UNICO model 2150 spectrophotometer was used for the absorption measurements; a Phoenix 986-AA type flame atomic absorption spectrophotometer was used for comparing the results and a Metrohm pH meter was used for measuring pH.

Reagents. All chemicals were of analytical reagent grade or the highest purity available, except SPAQ which was synthesized according to a method reported in the literature.[29] The procedure included diazotization of 4-aminobenzenesulfonic acid in ice-cold distilled water with sodium nitrite and coupling it to 8-aminoquinoline. The precipitate obtained was recrystallized and salted out with sodium chloride several times from water. The data obtained from NMR, FTIR, and UV–visible spectroscopy confirmed the SPAQ formation. About 2×10^{-4} M ($\text{M} = \text{mol dm}^{-3}$) SPAQ solution was prepared by dissolving 0.037 g of purified synthesized SPAQ in 500 mL of distilled water. 1000 $\mu\text{g mL}^{-1}$ Au^{III} solution was prepared by dissolving 0.145 g of $\text{H[AuCl}_4]\cdot x\text{H}_2\text{O}$ (49% Au) in a few mL of water and making up to 10 mL in a graduated flask. A 0.2% solution of cetyltrimethylammonium bromide (CTMAB) was prepared by dissolving 0.5 g of solid CTMAB in 250 mL of distilled water. Doubly distilled water was used throughout. Alumina (aluminum oxide anhydrous, γ-alumina) was activated with 4 M HNO_3 by shaking for a few seconds and rinsing with sufficient amount of distilled water for its neutralization was used for adsorption. All the reagents used were purchased from Merck (Darmstadt, Germany).

General Procedures. **Gold Adsorption on Immobilized SPAQ in a Column:** SPAQ solution (2×10^{-4} M, 3 mL) was added into a beaker containing 0.8 g of activated alumina particles and shaken for a few seconds. The adsorption capacity of SPAQ on alumina was determined to be 0.147 g per gram of alumina. 10–100 mL of gold stock solution containing 0.05–0.5 $\mu\text{g mL}^{-1}$ Au^{III} with pH 3–8 was passed through a column packed with SPAQ-coated alumina, with a flow rate of 2.5–5 mL min^{-1}. The column was then washed with 2 mL of distilled water and the adsorbed Au^{III} was eluted with 2 mL of 4 M HCl followed by 4 mL of distilled water to a 10-mL beaker containing 1.2 mL of CTMAB 0.2% and alkalinated by adding 2.3 mL of 4 M NaOH solution. After standing for 25 min the absorbance of final solution was measured at 611 nm.

Au–SPAQ Complex Adsorption on Alumina Column: To 10–100 mL of 0.05–0.7 $\mu\text{g mL}^{-1}$ Au^{III} solution in a 100-mL beaker; 3 mL of 0.2% CTMAB, and 2 mL of 2×10^{-4} M SPAQ solution were added in order, and alkalinated by adding 2 mL of 2 M NaOH. After 30 min standing for the complex formation, the solution was passed through a column (containing 1 g of activated alumina) at 2.5–5 mL min^{-1} flow rates. Preliminary experiments revealed that, if the column is treated with 0.01 M NaOH (2 mL) followed by rinsing with sufficient amount of distilled water, prior to the work, Au–SPAQ adsorption on the column was slightly increased. After washing the column with distilled water, the complex was eluted from the column with 3 mL of ethanol and the light absorption was immediately measured at 611 nm.

Determination of Au^{III} in Azerbaijan Ores. 5 g of crushed ore sample was transferred into a 250-mL beaker containing 50 mL of concentrated hydrochloric acid. The beaker was covered and heated gently on an electric heater to dissolve the sample. The mixture was filtered, the residue was mixed with 5 g of sodium peroxide, 2 g of sodium hydroxide, and fused (in a porcelain crucible) at 700 °C. The fused sample was washed with distilled water into a 250-mL beaker and 50 mL of concentrated hydrochloric acid was added. The mixture was heated to decrease the volume and then compensated with distilled water. Evaporation followed by distilled water addition was repeated several times. Remaining solution was transferred into a 100-mL flask and filled with distilled water. In gold determination using the first procedure, a needed volume of sample was passed through the column, containing 0.8 g of SPAQ-coated alumina, and eluted with 2 mL of 4 M HCl into a beaker containing 1.2 mL of 0.2% CTMAB and 2 mg of solid EDTA (disodium ethylenedinitrilo-*N*,*N*,*N*′,*N*′-tetraacetate: Na_2edta), as masking agent for Cu^{2+} ion. After alkalination of the solution with NaOH, the absorbance was measured at 611 nm. In similar methods reported in the literature, it is necessary to add a masking agent such as NaF to eliminate Fe^{3+} ion interference[29] but with our procedure, Fe^{3+} ions up to 150 $\mu\text{g mL}^{-1}$ did not interfere with the determination of 0.3 $\mu\text{g mL}^{-1}$ of Au^{III}. In higher concentrations of Fe^{3+}, addition of NaF seems to be required. In gold determination in ores using the second procedure, an appropriate volume of sample was transferred to a beaker containing 3 mL of 0.2% CTMAB, 2 mL of 2×10^{-4} M SPAQ, 5 mL of 5% NaF, and 6 mL of 2% EDTA solution and alkalinated with 2 mL of 2 M NaOH solution. After standing for 30 min, the complex formed was passed through a column containing 1 g of activated alumina. The adsorbed complex was then eluted from the column with 3 mL of ethanol followed by immediate absorption measurement at 611 nm.

Results and Discussion

Immobilization of SPAQ on Alumina for Au^{III} Adsorption. Mixing 2 mL of 2×10^{-4} M SPAQ, 1 mL of 0.2% CTMAB, and 1 g of alumina powder in alkaline media showed strong adsorption of SPAQ on alumina. Since Au^{III} solution is acidic, the procedure was repeated in acidic media (by adding 1 mL of 2 M HCl). Even after stirring for five minutes, no considerable adsorption was observed. An SPAQ solution containing an anionic surfactant, sodium dodecylsulfate (SDS), mixed with alumina powder showed enhanced adsorption of SPAQ. However, light absorption at 611 nm by Au–SPAQ in the presence of SDS has been reported to be lower in the absence of SDS.[29] Thus, SPAQ was immobilized directly on alumina without using any surfactant. Mixtures of 1 g of alumina powder, and 3 mL of 2×10^{-4} M SPAQ solution with different concentrations of NaOH, were shaken in a shaker for a few minutes, however, no adsorption of SPAQ on alumina was observed. The same procedure was repeated with acidic solutions with pH (1–5). Maximum adsorption was observed for a mixture of 5 mL of 2×10^{-4} M SPAQ and 2 mL of 0.2 M HCl solution, pH 2.6, and 1 g of alumina. The pH of the solution was changed to 4.6 after SPAQ adsorption on alumina. The color of SPAQ solution is orange in pH above 3.6 where most of SPAQ is in basic form (A^-), and red at pH below 3.6 where most of SPAQ is in acidic form (HA). Decoloration of the solution accompanied by conversion of the alumina color from white to orange indicates almost complete adsorption of the ligand (A^- form). In other words, the alumina surface which becomes positively charged by adsorbing proton at lower pH has strong affinity for SPAQ in A^- form but not for HA form.

Figure 1 shows SPAQ spectra in three pH values (2.5, 6, and 9.5). As shown in the figure spectra are similar in pH 6

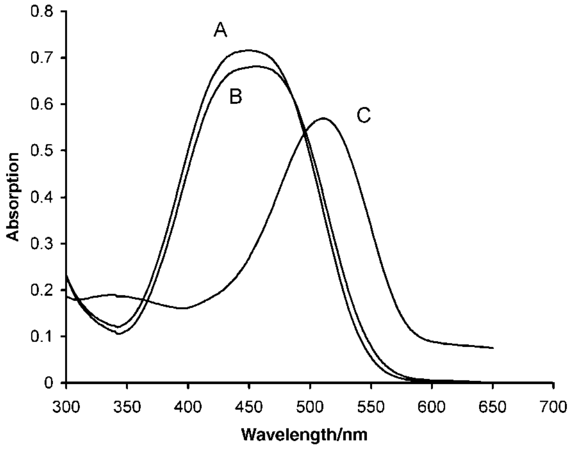

Figure 1. Absorption spectra of SPAQ solution using distilled water as a blank: A, pH 6; B, pH 9.5; and C, pH 2.5. Concentration of SPAQ solution is 5×10^{-5} M in A and B and 1×10^{-4} M in C.

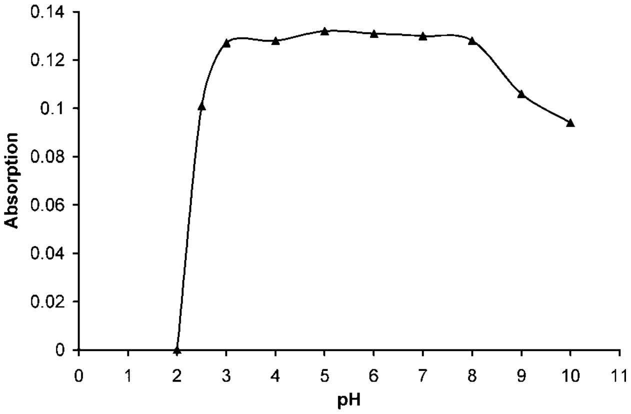

Figure 2. Effect of solution pH on adsorption of Au^{III} on SPAQ-coated alumina. 50 mL of 0.1 µg mL^{-1} Au^{III} solution at different pH values, 0.8 g of SPAQ-coated alumina. Elution and determining conditions are as described in Experimental section.

and 9.5 but in pH 2.5 the maximum absorbance shifted to a longer wavelength. This is expectable because the pK_{a3} of SPAQ is 3.65 ± 0.03 based on the literature.[29]

Adsorption of Au^{III} on SPAQ-Coated Alumina. The pH of Au^{III} solution is an important factor affecting adsorption of Au^{III} on SPAQ-coated alumina. Standard solutions with different pH but the same concentration of Au^{III} passed through a column packed with alumina (Experimental section) for Au^{III} adsorption. The results (Figure 2) indicated that for solutions of pH 3–8, Au^{III} is retained constantly on the column. It was also shown that below pH 2, SPAQ can not be adsorbed on alumina (above section) while above pH 8, since the alumina surface is negatively charged, and is not capable of SPAQ adsorption.

Elution of Adsorbed Au^{III} from SPAQ-Coated Alumina. Desorption of Au^{III} from SPAQ-coated alumina was studied by using different eluants. Common solvents such as acetone and alcohol did not prove to be suitable eluants. Sodium hydroxide solution and ammonia water were tested as available bases and their effectiveness was found to be very low. Because of the existence of the chloride form of Au^{III} in the sample hydrochloric acid was used as desorbing agent. It was observed that the recovery increased with increase in the concentration of HCl and remained constant in concentrations greater than 4 M HCl.

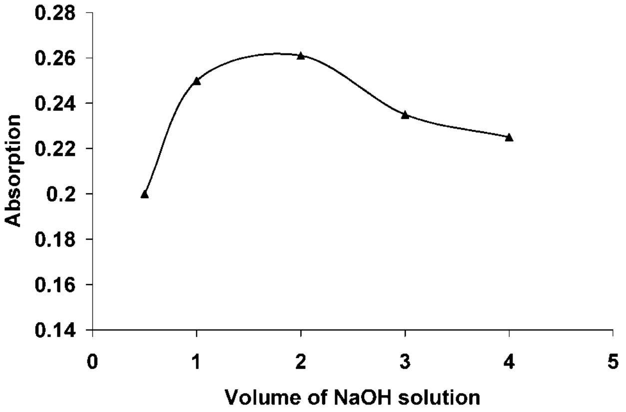

Figure 3. Effect of volume of NaOH solution (2 M) on formation and adsorption of Au–SPAQ complex.

Adsorption of Au–SPAQ Complex on Alumina. Au–SPAQ complex formed in alkaline media showed a strong affinity for adsorption on alumina. Solutions containing 50 mL of 0.2 µg mL^{-1} Au^{III}, 3 mL of 0.2% CTMAB, and 2 mL of 2×10^{-4} M SPAQ, alkalinated by adding 0.5–4 mL of 2 M NaOH solution, passed through a column packed with activated alumina. The result obtained indicated that maximum adsorption was achieved with 2 mL of 2 M NaOH solution (Figure 3). It was also shown that the complex adsorption on alumina decreases by adding more than 2 mL of 2 M NaOH. The adsorption efficiency of Au–SPAQ on the column at the optimum conditions was found to be 96.5–97.8%.

Elution of the Adsorbed Au–SPAQ Complex from the Alumina Column. A series of elute solutions were used in order to find a selective elute for desorption of Au–SPAQ complex. Some of the eluting agents used were based on former experiences in our laboratory.[14–18] 50 mL of 0.3 µg mL^{-1} Au^{III} solution was transferred into a beaker containing 3 mL of 0.2% CTMAB and 2 mL of 2×10^{-4} M SPAQ solution and alkalinated with 2 mL of NaOH solution. After standing for 30 min, the formed complex was passed through a column, containing 1 g of activated alumina. 2 mL of portions of listed eluants (Table 1) were used for desorbing Au–SPAQ complex. The absorbance of eluted solutions was measured at 611 nm and the percent recoveries of gold with respect to its adsorption efficiency (96.5–97.8%) were calculated by comparing with the absorbance of the same solution without passing through the column. The effect of ethanol as the best eluant (Table 1) was also examined. The results indicated that 97.1–98.4% recoveries can be obtained with 3 mL or more of ethanol if it was added in three 1 mL of portions followed by distilled water (1 mL) after each portion.

Optimization of Other Parameters. There were some other parameters to be optimized such as sample flow rate, amount of alumina loaded in the column, quantities of CTMAB and SPAQ, and standing time for reading the complex absorbance in the first procedure. For parameters like

Table 1. Recovery of Au–SPAQ Complex Extracted from the Column Containing Alumina with Different Elutes

Solvent	Recovery of Au–SPAQ/%
Acetone	0
Acetone/HCl (1 M) (1:3)	10.3
Hexane	0
Ethanol	88
Acetonitrile	71
Ethanol/Acetonitrile (4:1)	79
$\mathrm{H_2O}$/Ethanol (1:1)	0
HCl (1 M)	36
Methanol	46.5
Propanol	72.5
Ethanol/Methanol (1:1)	41.2
Acetone/Ethanol (1:3)	46.5
HCl (1 M)/Ethanol (1:1)	41.5
HCl (0.1 M)/Ethanol (1:20)	83

Table 2. Tolerable Concentration Ratios for the Spectrophotometric Determination of 0.3 μg mL^{-1} of $\mathrm{Au^{III}}$ with Proposed Procedure (Relative Error ±5%)

Ion added	Tolerable concentration ratio
$\mathrm{NO_3}^-$	2000
$\mathrm{Pb^{2+}}$, $\mathrm{Ba^{2+}}$, $\mathrm{Ag^{+}}$,a) $\mathrm{Fe^{3+}}$	1000
$\mathrm{Cl^-}$, $\mathrm{Ni^{2+}}$, $\mathrm{Hg^{2+}}$, $\mathrm{Na^{+}}$, $\mathrm{Fe^{3+}}$	500
$\mathrm{Al^{3+}}$	300
$\mathrm{Mg^{2+}}$, $\mathrm{Zn^{2+}}$, $\mathrm{Cd^{2+}}$	200
$\mathrm{Ca^{2+}}$, $\mathrm{Co^{2+}}$, $\mathrm{Cr^{3+}}$	100
EDTA	50
$\mathrm{F^-}$	20
$\mathrm{Cr^{VI}}$, $\mathrm{Pd^{2+}}$, $\mathrm{Pt^{IV}}$	10
$\mathrm{Cu^{2+}}$	5

a) Masked with 10 mg of NaF added to beaker containing desorbed $\mathrm{Au^{III}}$.

pH of the complex solution, amount of CTMAB, amount of alumina loaded in the column, and volume of ethanol in the second procedure, they were optimized employing procedures described earlier. It was found that the 0.8 and 1 g of alumina is the optimum amount for the first and second procedures respectively. The flow rates of 2.5–5 mL min^{-1} were optimum for both procedures. Volume of 3 and 2 mL of 2×10^{-4} M SPAQ and 1.2 and 3 mL of 0.2% CTMAB was found as optimum volumes of ligand and surfactant for the first and the second procedures respectively. It was also found that, desorption of the complex from the column was maximum if 3 mL of ethanol is used and the maximum absorbance at 611 nm is achieved in 25 min standing after NaOH addition in the first procedure.

Analytical Parameters. Under the optimum conditions, calibration graphs were obtained for $\mathrm{Au^{III}}$ determination by using a series of six standard solutions in both procedures. In the first procedure, the calibration graph was found to be linear in the range 0.05–0.50 μg mL^{-1} of $\mathrm{Au^{III}}$. The relative standard deviation (RSD) calculated for five replicate determinations of 50 mL of 0.2 μg mL^{-1} of $\mathrm{Au^{III}}$ was 3.01%. The limit of detection (LOD) based on IUPAC definition ($C_{\mathrm{LOD}} = 3S_{\mathrm{b}}/m$, where S_{b} is the standard deviation of blank, and m denotes the slope of the calibration line) was found to be 1.30 μg L^{-1}. For the second procedure, linearity of the calibration graph was in the range of 0.05–0.70 μg mL^{-1} of $\mathrm{Au^{III}}$. The RSD for 50 mL of 0.2 μg mL^{-1} $\mathrm{Au^{III}}$ was 2.66% based on five replicated measurements and the estimated LOD value was 3.70 μg L^{-1}.

Interferences. Preconcentration and separation of elements can be affected by the matrix constituents of the sample, so the influence of some ions on the preconcentration and determination of gold was examined. The ions tested were added individually to a 0.3 μg mL^{-1} solution of $\mathrm{Au^{III}}$ and passed through a column containing SPAQ-coated alumina. A maximum error of 5% in the absorbance reading was considered tolerable. The results of interference studies are presented in Table 2. The results indicated that $\mathrm{Cu^{2+}}$ was the major interferant, while $\mathrm{Cr^{VI}}$, $\mathrm{Pt^{IV}}$, and $\mathrm{Pd^{II}}$ interfere to a lesser extent. Interference of $\mathrm{Cu^{2+}}$ was eliminated by adding chelating agent, EDTA (disodium ethylenedinitrilo-*N*,*N*,*N′*,*N′*-tetraacetate: $\mathrm{Na_2}$edta), into eluted sample solution. The real sample (ore) used for analysis did not contain $\mathrm{Cr^{VI}}$, $\mathrm{Pt^{IV}}$, and $\mathrm{Pd^{II}}$ above the tolerable levels listed in Table 2.

Applications. The applicability of the proposed procedures for determination of gold in ores of Azerbaijan was examined. For Au, the most common AAS method is the extraction of $\mathrm{Au^{III}}$ by methyl isobutyl ketone (MIBK) from aqueous solutions of HCl and subsequently determination of the analyte by FAAS and GFAAS.[32,33] For the FAAS method three replicates were used, obtaining an average of 0.735 μg mL^{-1} with a standard deviation of 0.055. For the first and second procedures three replicates were carried out obtaining averages of 0.695 and 0.702 μg mL^{-1} with standard deviations of 0.081 and 0.063, respectively. The results obtained by the proposed procedures were compared with FAAS standard method by two-sided *t*-test. Statistical comparison at the 95% confidence level showed no significant difference between the results obtained with the proposed procedures and those of the FAAS standard method.

Conclusion

A method using alumina as a substrate for a solid-phase extraction has been developed for determination of $\mathrm{Au^{III}}$. The two proposed procedures provide a simple, sensitive, and inexpensive method for separation and preconcentration of μg L^{-1} amount of gold from ore samples. Utilizing the first procedure, $\mathrm{Au^{III}}$ can be determined in the presence of $\mathrm{Fe^{3+}}$ without any need for masking agent. In higher concentrations of $\mathrm{Fe^{3+}}$, addition of NaF seems to be necessary.

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