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Cyanotype Formula T

Preliminary version, November 10, 2026

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Preliminary potassium removal by tartrate precipitation: an alternative to Ware's method for conserving photosensitive iron(III)

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Abstract

This communication describes Cyanotype Formula T, an experimental process for the preliminary removal of part of the potassium from potassium ferricyanide by tartrate precipitation. The aim is to obtain, in situ, a solution in which the ferricyanide ion is predominantly associated with ammonium ions, without using photosensitive iron(III) as an agent in the separation. Unlike the approach adopted in Mike Ware's New Cyanotype, potassium is removed before ammonium iron(III) oxalate trihydrate is introduced.

Preparation in a small volume of solvent, without subsequent evaporation, yields 15.8 g of dry potassium-containing tartrate precipitate. The presence of potassium is confirmed qualitatively by a flame test on a washed and dried sample. The sensitizer, prepared using 20 g of the iron(III) complex per initial 10 g of potassium ferricyanide and diluted to 125 mL, produces prints of high visual density in the initial trials, with results considered comparable to those obtained by Ware's process. Performance, stability, and the composition of the precipitate require further investigation.

Introduction and aims of the study

This article is preliminary in nature. The present version brings together the origin of the hypothesis, the experiments, and the initial photographic results. Further data are needed on sensitivity, the characteristic curve, maximum density, sensitizer shelf life, and preparation variants. The observations do not constitute a conclusive validation of the formula.

This study does not claim to improve upon Mike Ware's remarkable New Cyanotype process or to challenge its underlying principles. Its sole purpose is to investigate an alternative means of achieving one of its chemical objectives: reducing the potassium introduced with ferricyanide and thereby generating, in situ, a solution containing predominantly ammonium ferricyanide.[1]

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Why remove potassium? Alkali-metal cations, particularly K^+, can be incorporated into the Prussian blue formed during cyanotype printing. The forms historically described as "soluble Prussian blue" are not truly water-soluble; rather, they have a greater tendency to undergo colloidal dispersion, or peptization. During washing, such dispersion can lead to pigment loss, reduced density, and sometimes unwanted migration of colour. Ware shows that favouring forms of the pigment associated with ammonium ions can limit these effects.[2]

In New Cyanotype, however, potassium is removed through the crystallization of potassium iron(III) oxalate trihydrate, $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$. The reaction separates the unwanted cation but also carries into the solid phase some of the iron(III) oxalate complex that could otherwise contribute to the photosensitive component.[3]

The experimental question therefore arises: can potassium be precipitated with an anion other than oxalate, avoiding the consumption of the photosensitive iron(III) component?

Origin of the hypothesis: tartrate crystallization in wine

The idea originates in a familiar oenological procedure: cold tartrate stabilization. Wine contains potassium and tartaric acid, which can form potassium hydrogen tartrate, $KHC_4H_4O_6$, a sparingly soluble salt commonly separated by cooling and filtration. The OIV's oenological standards recognize cold crystallization as a means of removing tartrates; the solubility of this salt in water is approximately 5.2 g/L at 20 °C.[4]

Winemaking practice uses temperatures close to the freezing point of wine, depending on the composition of the hydroalcoholic medium. By analogy, an aqueous ferricyanide solution might also allow K^+ to be separated as hydrogen tartrate. In the concentrated experiment, the mixture is cooled to approximately 1 °C.[5]

These conditions do not reproduce those found in wine, but exploit the same principle of decreasing solubility upon cooling.

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Chemical basis: in situ formation of ammonium ferricyanide

Ware's approach and the one proposed here share the same intended outcome: to reduce the proportion of K^+ and leave the hexacyanoferrate(III) ion, $[Fe(CN)_6]^{3-}$, in solution predominantly associated with NH_4^+. The difference lies in the salt through which potassium is removed.

Separation according to Ware (idealized scheme)

$$K_3[Fe(CN)_6] + (NH_4)_3[Fe(C_2O_4)_3] \rightleftharpoons (NH_4)_3[Fe(CN)_6] + K_3[Fe(C_2O_4)_3] \downarrow$$

Proposed tartrate separation

$$H_2Tar + NH_3 \rightleftharpoons NH_4^+ + HTar^-$$

$$K^+ + HTar^- \rightleftharpoons KHTar \downarrow$$

$$K_3[Fe(CN)_6] + 3\ NH_4HTar \rightleftharpoons (NH_4)_3[Fe(CN)_6] + 3\ KHTar \downarrow$$

In this representation, H_2Tar denotes tartaric acid and $HTar^-$ the hydrogen tartrate ion. The balance is idealized: it does not imply quantitative exchange or the presence of a single isolable salt in the liquid phase. In solution, potassium and ammonium ions coexist as charge-balancing cations; referring to the product as "ammonium ferricyanide" is therefore an operational description of its expected composition, not an analytical claim of purity.

The mole fraction of $HTar^-$ reaches its theoretical maximum at approximately pH 3.66, the mean of the two pK_a values of tartaric acid. This provides the rationale for the initial choice of a pH near 3.5–3.7, but does not establish that this range necessarily maximizes precipitation in the actual system.

First experiment: G-5, dilute procedure

The first formulation, recorded as G-5 in the laboratory notebook, uses 5.00 g of potassium ferricyanide, 6.84 g of tartaric acid, and approximately 6.8 mL of 10% aqueous ammonia. Tartaric acid is dissolved in 300 mL of demineralized water and partially neutralized to a pH of approximately 3.5; the ferricyanide is dissolved separately in 30 mL of water. The ferricyanide solution is added to the solution containing tartaric acid and ammonium ions.

Both solutions are initially clear. Following mixing, fine, sparkling crystals progressively nucleate and subsequently settle. Approximately 7 g of dry precipitate are recovered; losses during washing are not quantified. The formation of a solid phase even

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in a dilute solution is consistent with the precipitation of potassium hydrogen tartrate, although the composition is not determined quantitatively. A flame test performed on a washed and dried sample of the precipitate qualitatively confirms the presence of potassium.



Figure 1. G-5 experiment, from left: (a) solution following tartrate precipitation; (b) washed and dried precipitate; (c) flame test performed on the precipitate, showing the characteristic emission of potassium.

The limitation of this initial procedure is not the separation of the solid, but the need to reduce the volume of the solution subsequently. During heating to no more than approximately 50 °C, the liquid changes from bright yellow to a very dark reddish brown, almost black, although the loss of water is negligible. The change in colour therefore cannot be explained simply by increased concentration.

The nature of this transformation remains unknown. The literature describes iron(III)–tartrate complexes whose speciation also depends on pH; Bayer (1964) reports marked darkening during concentration at moderate temperature in an alkaline iron(III)–tartrate system.[6] The conditions are not directly comparable, however: in G-5, the iron initially present belongs to the ferricyanide ion. The similarity in colour therefore demonstrates neither the release of iron(III), nor the formation of iron–tartrate complexes, nor decomposition of hexacyanoferrate. Secondary reduction of ferricyanide likewise remains only a hypothesis.

Since it is not possible to establish whether the ferricyanide remains chemically unchanged, this solution is not used for photographic tests. The subsequent modification eliminates evaporation entirely.

Second experiment: G10-N, preparation in a small volume

The subsequent formulation, designated G10-N in the laboratory notebook, is prepared directly in a small volume and uses a different sequence of reagent addition. It is

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therefore not simply a doubling of G-5: precipitation takes place without any need for subsequent evaporation.

Potassium ferricyanide is dissolved in approximately 50 mL of demineralized water, after which 10% aqueous ammonia is added. Tartaric acid, previously dissolved in approximately 25 mL of demineralized water, is then introduced gradually. Throughout this addition, the ferricyanide is thus present in an ammonia-containing solution.

Until approximately 70–80% of the tartaric acid has been added, the mixture shows no evident macroscopic change. Beyond this point, a copious, finely divided, milky-white suspension suddenly appears, markedly different from the sparkling crystals observed in G-5. Its morphology suggests faster nucleation, but does not in itself identify the solid phase.

The mixture is cooled to approximately 1 °C and filtered. Approximately 60 mL of clear, bright yellow solution are obtained; the washed and dried precipitate weighs 15.8 g. Washing entails unquantified losses of solid material and may also remove some of the ferricyanide solution retained by the precipitate.

A flame test on a washed and dried sample of the precipitate qualitatively confirms the presence of potassium. From the initial 10 g of potassium ferricyanide, the calculated stoichiometric maximum is 17.14 g of pure potassium hydrogen tartrate. The recovered mass of 15.8 g is consistent with substantial separation, but does not measure the fraction of K^+ removed: ammonium hydrogen tartrate may also be present in the solid.

Preparation and conditioning of the sensitizer

Separately, 20.00 g of ammonium iron(III) oxalate trihydrate, $(NH_4)_3[Fe(C_2O_4)_3]\cdot 3H_2O$, are dissolved in approximately 40 mL of demineralized water. The resulting solution is added to the ferricyanide solution from which potassium has been partially removed. The mass ratio of the iron(III) complex to the initial potassium ferricyanide is 2:1, compared with the starting ratio of 3:1 in Ware's process.[7]

The mixture becomes very dark green, without immediate crystalline precipitation. After standing, a small amount of blue deposit appears, visually consistent with Prussian blue, and is removed by a second filtration. The volume of the filtered solution is approximately 100 mL.

Initial coatings made with this solution nevertheless exhibit localized circular irregularities. Their appearance suggests the formation of surface crystallization nuclei during drying, possibly due to residual potassium hydrogen tartrate. The identity of the deposit remains unconfirmed.

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To eliminate these irregularities, the solution is diluted from approximately 100 to 125 mL with demineralized water. This dilution is therefore an integral part of the formulation used in the subsequent photographic tests.

Initial photographic results

Prints produced with Formula T diluted to 125 mL exhibit high visual density, a broad tonal range, and excellent separation of blue tones, particularly in the transitions between deep shadows, midtones, and highlights. In the trials conducted so far, their photographic performance is judged to be closely comparable to that of Ware's New Cyanotype. Preliminary toning tests with lead acetate also demonstrate a favourable response, with a marked change in colour while preserving fine detail and tonal gradation.

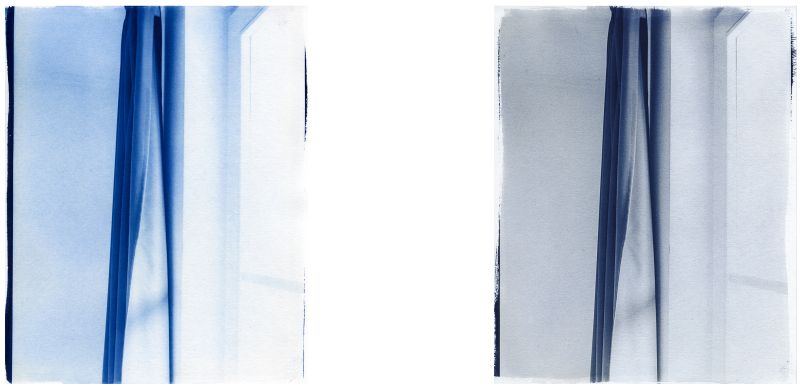

Figure 2. Cyanotype prints produced with Formula T (125 mL final sensitizer volume). Left: untreated print, showing a broad tonal range and fine separation of blue tones. Right: the same image toned with lead acetate, demonstrating the response of the pigment to chemical toning and the preservation of tonal detail.

No evident lateral migration of pigment, or bleeding sufficient to impair fine detail, is observed.

The acidified wash bath takes on a greenish-blue colour, indicating dispersion of some coloured material, without an obvious deterioration in the observed final density. One possible explanation is the removal of pigment deposited on the surface or weakly retained by the paper fibres; the actual distribution of the pigment and the extent of these losses remain to be established.

The comparison with Ware's process remains visual rather than densitometric. The disappearance of coating irregularities after dilution, by contrast, constitutes an observed practical result.

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Economy of iron(III) and interpretative limitations

The distinguishing feature of Formula T is not an attempt to remove K^+ quantitatively, but to separate a substantial fraction of it before introducing the photosensitive iron(III) component. In a nominal comparison based on an initial 10 g of potassium ferricyanide, Formula T uses 20 g of ammonium iron(III) oxalate trihydrate versus 30 g in Ware's formulation: a 33.3% reduction in the starting mass of this reagent. This difference does not automatically imply identical final compositions, since the amount of ferricyanide retained may also change during tartrate separation.

The potassium-containing precipitate and the photographic response support the feasibility of the principle. The composition of the solid (KHTar/NH_4HTar), the actual proportion of K^+ removed, the pH after precipitation, and the nature of the blue deposit formed after addition of the iron(III) complex remain undetermined.

The reddish-brown colour change in heated G-5 remains without a definitive explanation. Studies of iron(III)–tartrate coordination document strongly coloured species, but do not demonstrate ferricyanide decomposition under the conditions examined here.[8] Colour alone cannot establish the formation of such complexes or the fate of the ferricyanide ligands; for this reason, the final procedure avoids heating.

Conclusion

The initial trials show that tartrate precipitation may provide a practical alternative to potassium removal through potassium iron(III) oxalate trihydrate, as used by Ware. Both approaches aim to favour ferricyanide in an ammonium-rich solution, but in Formula T the separation takes place before the photosensitive iron(III) is introduced.

G10-N yields 15.8 g of dry potassium-containing tartrate precipitate and a sensitizer which, following the addition of 20 g of ammonium iron(III) oxalate trihydrate and dilution to 125 mL, produces prints of high visual density, preliminarily comparable to those obtained with Ware's process.

The result does not establish superiority over New Cyanotype; rather, it indicates the possibility of reducing consumption of the photosensitive iron(III) component through a preparation accessible to an ordinary photographic darkroom. Quantitative performance and shelf-life assessments remain subjects for further experimentation.

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