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Silver Extraction for Pollution Control of Photographic Fixing Solution with Tetramethylthiuram Disulfide

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Silver recovery from photographic fixing solutions can be performed by solvent extraction with thiuram disulfides. Tetramethylthiuram disulfide (TMTDS) was selected for further studies because it had the highest distribution ratio among the three extractants. Its selectivity for silver extraction from a thiosulfate medium and from an analytical photographic fixing solution were evaluated. A 1 : 1 silver(I)–TMTDS complex is formed. For a one-stage and one-hour silver(I) extraction process, a 96% recovery was obtained from an analytical fixing solution containing 1 g dm^{-3} silver(I), starting with a 0.02 M (1 M = mol dm^{-3}) TMTDS solution. The possible extraction mechanism involves the reduction of TMTDS in the presence of thiosulfate ions, followed by chelation of the silver(I) with the reduced TMTDS. Effective stripping can be performed by using 3 M hydrochloric acid. By dilution of the fixing solution with water (1 : 1), and the use of 0.1 M TMTDS, recycling of the organic phase between the extraction and stripping stages for silver extraction can be achieved in a few times. The results for the analytical solutions were further shown to be applicable to a black and white photographic industrial solution.

Silver is the element used as the light sensitizing agent in most photographic and X-ray materials and is thus widely available for recovery. The excess of non-reacted silver halide is normally dissolved in a sodium or ammonium thiosulfate fixing solution. Direct emission of this solution to the environment is undesirable because of the presence of a number of harmful components. Regulations for recomended allowable silver discharge levels from 0.1—1.0 mg dm^{-3} are expected.[1)] From an environmental point of view, the best way of reducing the undesirable wastes would be to reuse the major part of the fixing solution or to recover the silver from the waste solution. Normally, the recovery of silver is profitable at high concentrations while a reduction to low concentration is far more difficult.[1,2)] The silver is recovered either by electrolysis, adsorption, cementation, sulfide precipitation, ion exchange, or solvent extraction.[3)] However, all of these processes possess limitations either from environment or technical points of view.[1,2)]

So far, work performed on evaluating solvent extraction techniques for thiosulfate solutions is limited to amine extractants.[3—7)] Amines require the formation of an amine salt with a mineral acid in order to be an effective extractant. Still only moderate extraction was measured from these solutions. In addition, the thiosulfate concentration required at the stripping stages needs to be 2—3 M, which could be a hindrance for the electrolytical silver recovery.

The silver(I) ion would also be readily extracted with a dithiocarbamate. It is well known that *N*,*N*-diethyldithiocarbamate forms complexes with many metal ions as a non-selective complexing agent,[8)] but the thiuram sulfides which contain two moieties of dithiocarbamates would be expected to exhibit an enhanced selectivity toward metal ions due to the appropriate positions of the two dithiocarbamate groups. Further, the sodium salt of *N*,*N*-diethyldithiocarbamate is less soluble in organic solvents, while thiuram sulfides are easily soluble in organic solvents. Thiuram sulfides make a useful alternative to the sodium salt of *N*,*N*-diethyldithiocarbamate, where it can be used to extract metal from the aqueous phase.

This work is devoted to the problem of silver reduction in the fixing solutions. Its aim is to investigate the extraction of silver(I) thiosulfate complexes using thiuram sulfides, such as tetramethylthiuram disulfide, in order to allow recycling of silver or discharge of the photographic fixing solution into the effluents.

Experimental

Reagents. All reagents used were of analytical grade. Silver nitrate dissolved in water was used for the aqueous silver solution. 1,2-Dichloroethane (DCE) was shaken with water before use. Decanol was used as additive in order to inhibit emulsion formation. The following thiuram sulfide extractants were used as supplied by the manufacturer; tetramethylthiuram disulfide (TMTDS) and tetraethylthiuram disulfide (TETDS) from Tokyo Kasei Kogyo and tetraisopropylthiuram disulfide (TiPTDS) from Aldrich Chemical Co., Inc. Other bis(dithiocarbamates) like 1, 1′-[dithiodi(thiocarbonyl)]dipyrrolidine (DTDTCDPr), methylene bis(*N*,*N*-diisobutyldithiocarbamate) (MBDiBDTC), 1,4-butanediyl bis(*N*,*N*-diethyldithiocarbamate) (BBDEDTC), 1,4-phenylenedimethylene bis(*N*,*N*-dimethyldithiocarbamate) (PhDMBDMDTC), and 1,4-phenylenedimethylene bis(*N*,*N*-diethyldithiocarbamate) (PhDMBDEDTC) were synthesized by similar methods described in previous reports.[9,10)] The products were purified by recrystallization or vacuum distillation. The identification of the products were carried out using elemental analysis. Some of the physical characteristics and results of the elemental analysis of the synthesized compounds were as follows:

DTDTCDPr. White crystals with mp 131.0—133.0 °C. Found: C, 41.03; H, 5.50; N, 9.52%. Calcd for $C_{10}H_{16}S_4N_2$: C, 41.06; H, 5.51; N, 9.68%.

MBDiBDTC. White crystals with mp 69.8—70 °C. Found: C, 53.96; H, 9.05; N, 6.65%. Calcd for $C_{19}H_{38}S_4N_2$: C, 53.98; H, 9.06; N, 6.63%.

BBDEDTC. White crystals with mp 80.1—81.0 °C. Found: C, 47.67; H, 8.06; N, 7.85%. Calcd for $C_{14}H_{28}S_4N_2$: C, 47.67; H, 8.00; N, 7.95%.

PhDMBDMDTC. White crystals with mp 170—172 °C. Found: C, 48.41; H, 5.78; N, 8.03%. Calcd for $C_{14}H_{20}S_4N_2$: C, 48.80; H, 5.85; N, 7.72%.

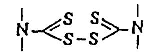
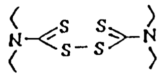
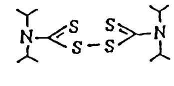
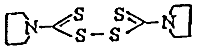
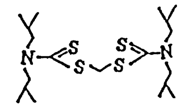
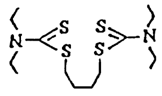
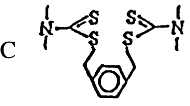
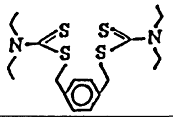
PhDMBDEDTC. White crystals with mp 75.2—76.2 °C. Found: C, 53.90; H, 7.02; N, 6.98%. Calcd for $C_{18}H_{28}S_4N_2$: C, 53.96; H, 7.04; N, 6.99%.

Procedure. In a 50 ml glass-stoppered cylindrical glass tube, 10 ml of the organic solvent containing the specific bis(dithiocarbamate) dissolved in DCE was added with 10 ml aqueous thiosulfate solution containing silver(I). The two phases were shaken at a predetermined time at 200 strokes min^{-1} at 25 °C. They were centrifuged for 5 min at 2000 rpm and then separated. The pH of the aqueous phase was measured. The pH adjustments were done by the addition of dilute sulfuric acid or sodium hydroxide solutions to the aqueous solutions. The concentration of silver(I) in the aqueous phase was measured by atomic absorption spectrometry using SAS 7500 A (Seiko Instruments Inc.). The combined organic phase was stripped with different back-extractants, after which the metal-free organic phase was reused for silver extraction. Again, the concentration of silver(I) in the aqueous phase after back-extraction was measured using the same method.

Result and Discussion

Table 1 shows the extraction efficiencies of some bis(dithiocarbamate) extractants for the extraction of silver(I) from thiosulfate medium. Selective extraction of silver(I) from thiosulfate solutions has not been exhaustively investigated due to the tight bonding between silver and thiosulfate ions. But, as shown in the results of Table 1, there is the capability of the thiuram disulfides to extract Ag(I) from the thiosulfate medium. In thiosulfate medium, tetraalkylthiuram disulfide is reduced to two dithiocarbamate ions in the presence of silver(I) ions, leading to the stable formation of tetrathionate ions and silver *N*,*N*-dialkyldithiocarbamate.[11] The reaction mechanism is explained in the later section. Increasing the size of the alkyl groups in the *N*,*N*-dialkyl dithiocarbamate should increase the lipophilic character in itself, and also through the resultant increased inductive effect on the electron density of the dithiocarbamoyl moiety, resulting in reduced ionization constants.[12] It should also decrease the electropositive character of the nitrogen atom and thus reduce the strength of the free acid.[13] The effect is seen in extractants **1**—**4**, which show that lengthening of the hydrocarbon chain reduces silver extractability. The high extractabilities of extractants **1**, **4**, and **7**, suggests that it is the inductive effect rather than the mesomeric effect which determines the relative magnitude of total electron release in the series.[14] The relative magnitude of electron release (inductive plus mesomeric) decreases in the order methyl > pyrrolidinyl > ethyl ≃ isopropyl groups. Independent work on *N*,*N*-dialkyldithiocarbamic acid derivatives showed the importance of the alkyl chain in the *N*,*N*-dialkyldithiocarbamate, which decreases rapidly on ascending the homologous series.[15—18] The presence of an alkyl chain between the two dithiocarbamate groups in extractants **5**—**8**, prevents the reduction of the bis(dithiocarbamate) molecule into dithiocarbamate ions, which explains the poor selectivity for silver(I). TMTDS appears to be the best extracting agent among the thiuram disulfides tested; and so, for the succeeding experiments, only TMTDS is considered.

Table 1. Extractabilty of Silver(I) with Bis(dithiocarbamate) Derivatives from Thiosulfate Medium

	Extractant	Ag Extraction / %
1 TMTDS		100
2 TETDS		18.3
3 TiPTDS		18.7
4 DTDTCDPr		84.6
5 MBDiBDTC		8.7
6 BBDEDTC		2.2
7 PhDMBDMDTC		32.1
8 PhDMBDEDTC		0

[Extractant] = 2.5×10^{-3} M, [Ag^+] = 1.0×10^{-4} M in 4.4×10^{-3} M $Na_2S_2O_3$, shaking time = 1 h.

The nature of the thiosulfate used, either $(NH_4)_2S_2O_3$ or $Na_2S_2O_3$, at $(1.0—3.0)\times10^{-4}$ M does not affect the extractability of silver(I) with the TMTDS. The extraction of silver(I) was further investigated at different thiosulfate concentrations. The results are shown in Table 2. At the thiosulfate concentrations equal to 5.0×10^{-5} M and below, the aqueous phase turned brown and precipitation occurs. At low concentrations of $(0.8—10.0)\times10^{-4}$ M $Na_2S_2O_3$, extractability is not affected by the concentration of sodium thiosulfate. A decrease in the extraction percentage is observed above 1.0×10^{-2} M $Na_2S_2O_3$ due either to the formation of non-extractable silver(I) thiosulfate complexes or coextraction of thiosulfate.[3] Thus, extractability is dependent on the concentration of the sodium thiosulfate.

The effect of shaking time is shown in Fig. 1. The extraction equilibrium was established in 50 min with 100% silver(I) extraction. Figure 2 shows the plot of log D vs.

Table 2. Effect of Thiosulfate Concentration on the Extractability of Silver(I) with TMTDS

$[Na_2S_2O_3]$ / M	Silver extraction / %
8.0×10^{-5}	100
1.0×10^{-4}	100
2.0×10^{-4}	100
3.0×10^{-4}	100
5.0×10^{-4}	100
1.0×10^{-3}	100
1.0×10^{-2}	93.2
1.0×10^{-1}	85.3
0.5	0
1.0	0

$[TMTDS]=2.0\times10^{-4}$ M, $[Ag^+]=1.0\times10^{-4}$ M, shaking time = 1 h.

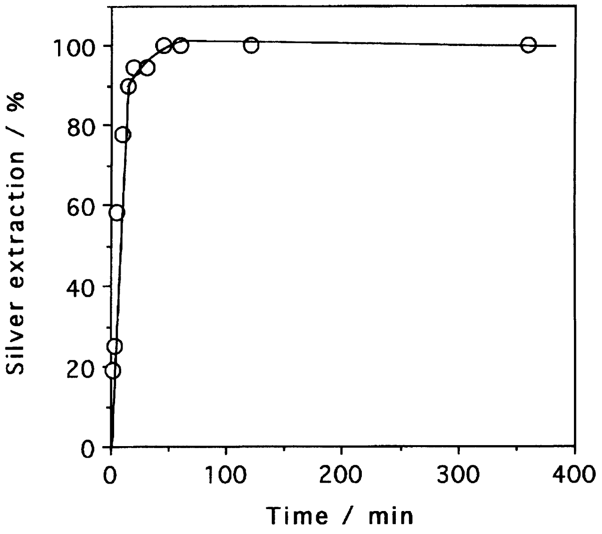


Fig. 1. Effect of shaking time on the extraction of silver(I) thiosulfate complex with TMTDS. $[TMTDS]=2.0\times10^{-4}$ M in DCE, $[Ag^+]=1.0\times10^{-4}$ M in 1.0×10^{-3} M $Na_2S_2O_3$.

log [L], where D is the distribution ratio and [L] is the ligand concentration. It gave a straight line with a slope of 0.96. This corresponds to the formation of a 1 : 1 silver(I) : TMTDS complex. Studies of the relationship between the degree of extraction versus the acidity of the aqueous phase are shown in Fig. 3, which indicated that maximum extraction was achieved at pH = 4.0 to 8.5. At the lower pH than 2.5—3.0, the TMTDS decomposes to form precipitates and volatile sulfur-forming compounds. At pH values greater than 8.5, the degree of extraction is diminished due to the formation of non-extractable Ag(OH).[19]

The silver(I) in the organic phase must be stripped (backed-extracted) to a suitable salt solution, from which silver(I) is readily recovered by electrolysis. A long chain alcohol was added to the solvent to prevent third phase formation,[3,4] and to enhance the back-extraction process. Figure 4 shows the effect of decanol concentration in the extraction and back-extraction of silver. The addition of decanol caused a slight decrease in the extractability of silver(I). But the formation of emulsion was hindered and a back-extraction process was possible. Using a 20% decanol with DCE as modifier was found to be the appropriate concentration for the extraction and back-extraction of silver. The results for a number of back-extractants are tabulated in Table 3. Thiourea is an effective stripping agent but, it is unstable upon long storage. On the other hand, no stripping is obtained with nitric acid, sulfuric acid, ammonium thiocyanate or sodium chloride. Hydrochloric acid had been a good stripping agent and was further tested for silver stripping at various concentrations Starting at 3 M HCl solution, it can strip more than 90% of the silver(I).

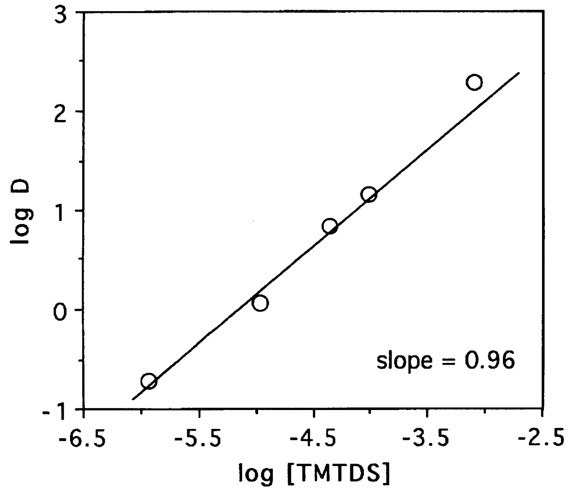


Fig. 2. Determination of stoichiometry of silver(I)–TMTDS complex by slope ratio method. $[Ag^+]=1.0\times10^{-4}$ M in 1.0×10^{-3} M $Na_2S_2O_3$, $[TMTDS]=0.8\times10^{-4}$—5.0×10^{-3} M in DCE, shaking time = 1 h.

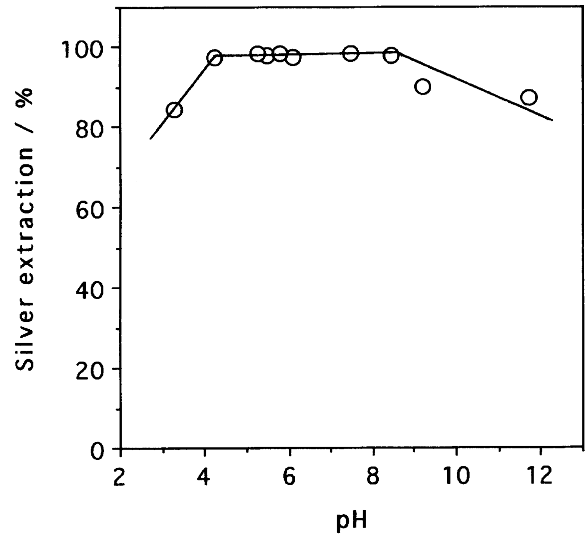


Fig. 3. Effect of pH on the extraction of silver(I)–thiosulfate complex with TMTDS. $[TMTDS]=2.0\times10^{-4}$ M in DCE, $[Ag^+]=1.0\times10^{-4}$ M in 1.0×10^{-3} M $Na_2S_2O_3$, shaking time = 1 h.

The extraction mechanism of silver(I) with TMTDS can be explained by the following reactions. In aqueous thiosulfate solution, $Ag(S_2O_3)_2^{3-}$ is formed.[4] In the presence

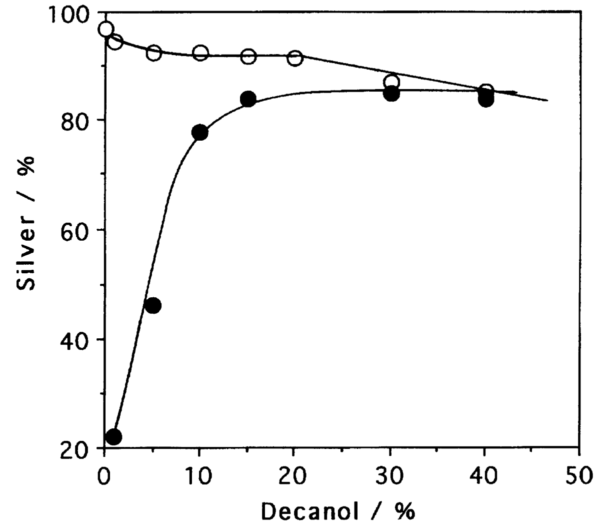


Fig. 4. Extraction and back-extraction of silver(I) at different modifier concentration. $[Ag^+] = 1.0 \times 10^{-4}$ M in 1.0×10^{-3} M $Na_2S_2O_3$, $[TMTDS] = 2.5 \times 10^{-3}$ M in decanol–DCE mixture, back-extractant = 5 M HCl, shaking time = 1 h per one process. (○) extraction, (●) back-extraction.

Table 3. Reagents used for Back-Extraction of Silver(I) from the Organic Layer

Reagent	Silver back-extracted / %
1 M HCl	79.7
3 M HCl	92.6
1 M HNO_3	0
1 M H_2SO_4	0
1 M NH_3	6.2
1 M NH_4CNS	0
1 M NaCl	0
5% Thiourea	91.4

$[TMTDS] = 2.5 \times 10^{-3}$ M in 20% decanol–DCE mixture, $[Ag^+]=1.0 \times 10^{-4}$ M in 1.0×10^{-3} M $Na_2S_2O_3$, shaking time=1 h.

of thiosulfate, the reduction of TMTDS and formation of the silver(I) *N,N*-dimethyldithiocarbamate complex occurs according to:[11)]

$$(CH_3)_2NCS_2S_2CN(CH_3)_2 + Ag(S_2O_3)_2{}^{3-} \rightleftharpoons [(CH_3)_2NCS_2\text{–}Ag\text{–}S_2CN(CH_3)_2]^- + S_4O_6{}^{2-}. \quad (1)$$

The Na^+ as the counter cation permits an easy formation of the silver(I) *N,N*-dimethyldithiocarbamate complex in the organic phase.

The extraction constant K_{ex} for Eq. 1 and the distribution ratio D of silver are defined as follows:

$$K_{ex} = \frac{[[(CH_3)_2NCS_2\text{–}Ag\text{–}S_2CN(CH_3)_2]^-][S_4O_6{}^{2-}]}{[(CH_3)_2NCS_2S_2CN(CH_3)_2][Ag(S_2O_3)_2{}^{3-}]}, \quad (2)$$

$$D = [[(CH_3)_2NCS_2\text{–}Ag\text{–}S_2CN(CH_3)_2]^-]/[Ag(S_2O_3)_2{}^{3-}]. \quad (3)$$

The concentration of the metal complex in the aqueous phase must be negligibly small, and thus the relationship between D and K_{ex}, can be given by a logarithmic expression as follows:

$$\log D = \log K_{ex} + \log [(CH_3)_2NCS_2S_2CN(CH_3)_2] - \log [S_4O_6{}^{2-}]. \quad (4)$$

The relationship between $\log D$ and $\log$ [TMTDS], as shown in Fig. 2, gave a slope of 1. Therefore in Eq. 1, only 1 mole of TMTDS is required to form the silver(I) complex.

There are two possible back-extraction processes. First, the mechanism involved when $[(CH_3)_2NCS_2\text{–}Ag\text{–}S_2CN(CH_3)_2]^-$ reacts with HCl[13,19,20)] is shown below:

$$[(CH_3)_2NCS_2\text{–}Ag\text{–}S_2CN(CH_3)_2]^- + 2\,HCl \rightleftharpoons AgCl_2{}^- + 2(CH_3)_2NCS_2{}^- + 2H^+. \quad (5)$$

And the other possibility is the reaction of $[(CH_3)_2NCS_2\text{–}Ag\text{–}S_2CN(CH_3)_2]^-$ with thiourea[21,22)] as follows:

$$[(CH_3)_2NCS_2\text{–}Ag\text{–}S_2CN(CH_3)_2]^- + CS(NH_2)_2 \rightleftharpoons 2(CH_3)_2NCS_2{}^- + NH_3 + H^+ + AgSCN. \quad (6)$$

As an application, the TMTDS was tested on a artificial solution (analytical photographic fixing solution) which contains buffering, antioxidizing species and silver salts as well as thiosulfate. From an analytical fixing solution, silver recovery of 100% was obtained starting with 0.01 M TMTDS, as presented in Fig. 5. The effect of shaking time on the extraction of silver(I) from an analytical fixing solution is shown in Fig. 6. The extraction was rapid, and equilibrium was attained in about 50 min. But, the presence of other species than silver and thiosulfate ions in the fixing solution may have interfered in the extraction rate, as indicated by a delayed deflection in the extraction curve during the first 5—20 min. These components must have caused some interfacial and hydrodynamic effects in the aqueous phase which delayed the transfer of Ag^+ into the organic phase to form the Ag(I)-TMTDS complex. Or TMTDS in the organic phase is

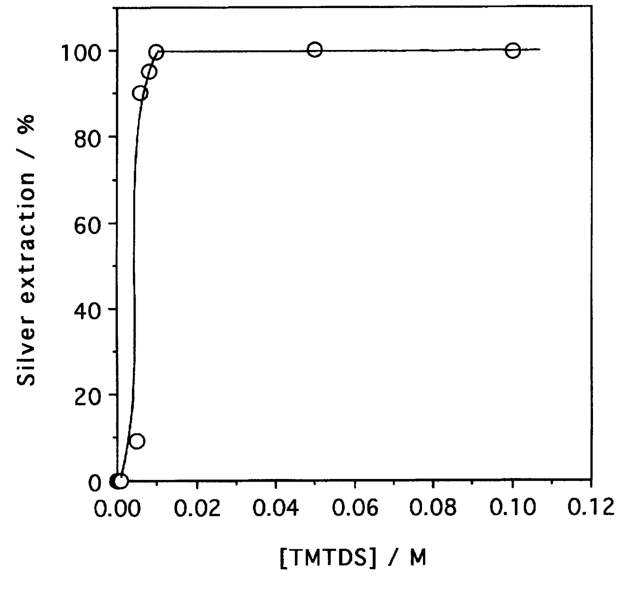


Fig. 5. Extraction of an analytical fixing solution with TMTDS. shaking time=1 h, composition of analytical fixing solution[1)] (0.5 M $Na_2S_2O_3$, 0.1 M H_3BO_3, 0.05 M CH_3COONa, 0.1 M $Na_2SO_3 \cdot 7H_2O$, 0.1 M CH_3COOH, 1 g dm^{-3} Ag).

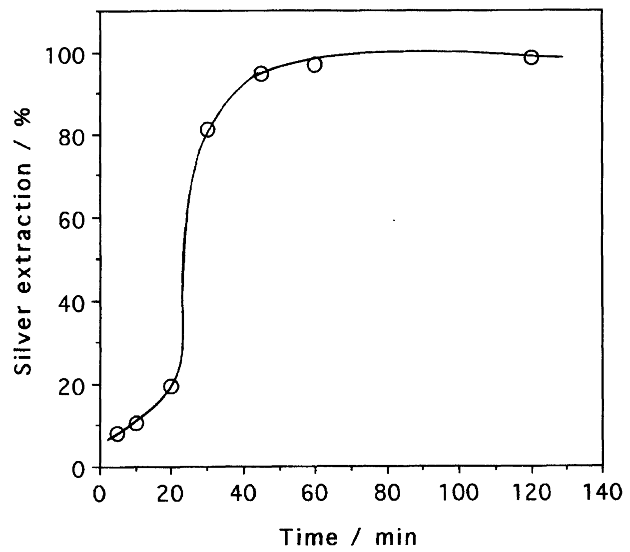


Fig. 6. Effect of shaking time on the extraction of silver(I) from the analytical fixing solution[a)] with 0.01 M TMTDS.
a) composition of solution is the same as in Fig. 5.

physically partitioned to the aqueous phase and is adsorbed at the interface. Then, TMTDS adsorbed at the interface undergoes the complex-formation with Ag(I).

The effect of various concentrations of TMTDS on the extraction and back-extraction of silver(I) from a fixing solution is presented in Table 4. The results shown in Table 4. A indicate that the TMTDS reagent probably decomposes in solutions at lower pH during the back-extraction process. Such that the metal-free organic phase after back-extraction was now a poor extractant, as evidenced by a very low silver(I) extractability during the second extraction process. In Table 4. B, TMTDS is not destroyed by the thiourea solution during the stripping process but the thiourea solution is not an effective stripping agent for silver(I) in the presence of a complex solution, as indicated by a poor silver(I) recovery after back-extraction. Results in Table4. A and B, again proved that 3 M HCl is a better back-extractant than with 5% thiourea. Decomposition of *N*,*N*-disubstituted dithiocarbamate under acidic conditions to amine and carbon disulfide is a very slow process.[13)] And therefore extractions at low pH should be performed immediately, preferably with excess of reagent present.[23)] Decomposition of the reagent was offset by the use of an excess amount of a diluted fixing solution; then, there is a low silver(I) ion concentration in the solution. The TMTDS was available for recycling, even after hydrochloric acid treatment. This is revealed by the high extractability of silver(I) in the second extraction of silver with 0.05 M and 0.1 M TMTDS from a diluted fixing solution at 1 : 1 ratio with water, as shown in Table 4.C.

TMTDS was further tested on an industrial solution. Two different solutions of a black and white photographic fixing solutions were used, without and with developer's solution. The initial silver(I) concentrations were 79.1 and 47.9 mg dm^{-3}, respectively. The results are shown in Table 5. Silver extraction is very effective for both solutions, while the results for the back-extraction process were lower as compared to the data of the diluted fixing solution treated with 0.1 M TMTDS in Table 4. One explanation for the lower recovery in these solutions is the chemical complexity of industrial solutions. Based from the results of the fixing solution with developer's solution, *p*-(methylamino)phenol sulfate and hydroquinone as the active ingredients[24)] of the developer's solution may have interfered in the silver recovery. Increasing the HCl concentration to 5 M during back-extraction is not advisable, even though it increases the efficiency of the silver stripping from the organic phase, because it also hastens the decomposition of the extractant.

In industrial solutions, the behavior is further complicated by complexation with other anions as well as co-extraction

Table 4. Extraction and Back-Extraction of Silver(I) with HCl and Thiourea Solution from a Fixing Solution[a)] at Various Concentration of TMTDS

Fixing solutions at different [TMTDS]	Silver / %		
	1st extraction	Back-extraction	2nd extraction
A. Undiluted fixing solution		(3 M HCl)	
0.02 M TMTDS	95.8	95.0	2.5
0.05 M TMTDS	95.6	98.6	2.3
0.10 M TMTDS	95.0	98.6	1.4
B. Undiluted fixing solution		(5% thiourea)	
0.02 M TMTDS	99.8	13.6	—
0.05 M TMTDS	99.4	14.2	—
0.10 M TMTDS	99.6	12.5	—
C. Fixing solution diluted with water (1 : 1)		(3 M HCl)	
0.02 M TMTDS	97.2	98.8	16.6
0.05 M TMTDS	96.7	100	92.7
0.10 M TMTDS	96.2	99.8	96.9

a) Composition of fixing solution is shown in Fig. 5, shaking time=1 h per process.

Table 5. Extraction and Back-Extraction of Silver(I) from a Black and White Photographic Fixing Solution

Photographic fixing solution	Silver / %	
	1st extraction	Back-extraction
	(0.1 M TMTDS)	(3 M HCl)
Without developer's solution	98.1	78.9
With developer's solution	97.3	53.3
		(5 M HCl)
Without developer's solution	97.9	88.4
With developer's solution	97.7	90.0

Original silver(I) concentration in fixing solution without developer's solution=79.13 mg dm^{-3} Ag, and in fixing solution with developer's solution=47.9 mg dm^{-3} Ag, shaking time=1 h per process.

and degradation products. It is estimated that by dilution of the fixing solution, recoveries of over 99% can be achieved even after back-extraction and second extraction processes.

Thiuram disulfides especially TMTDS, are an efficient extracting reagent for silver(I) contained in thiosulfate media. Solvent extraction techniques have further shown promising results for the silver recovery from an analytical fixing solution and industrial photographic black and white fixing solution by the use of TMTDS. However, for solvent extraction to be an attractive alternative to other silver recovery processes where environmental limits must be satisfied, further knowledge must be gathered about other complexation and degradation products.

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