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THE PHOTOGRAPHIC EMULSION: ANALYSIS FOR NONHALIDE SILVER AND SOLUBLE BROMIDE

By Burt H. Carroll and Donald Hubbard

ABSTRACT

This paper is a critical study of methods proposed for the determination in emulsions of silver in forms other than silver halide, and a description of a new method of extracting soluble bromide from emulsions. The method of Weigert and Lühr, based on double fixation with thiosulphate, is found to be reliable; the principal danger is decomposition of silver thiosulphate to sulphide. The method of Schmidt and Pretschner, direct extraction with nitric acid, is too insensitive. Soluble bromide may be quantitatively extracted from plates by three changes of dilute acid; error from formation of silver-gelatin complex is thus eliminated. Electrometric titration at pH2 or less may be used for liquid emulsions, and is preferable for analysis of plate extracts, but it is also possible in the latter case to determine the bromide by oxidation to cyanogen bromide, with subsequent iodometric titration, according to Lang.

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I. DETERMINATION OF NONHALIDE SILVER

1. INTRODUCTION

The existence in ripened silver bromide-gelatin emulsions of sensitivity nuclei attached to the silver bromide grains is now established so thoroughly that it need not be discussed. The mechanism of their action is outside the scope of this paper. We are here concerned with the methods proposed for the determination of nonhalide silver in emulsions, their reliability and accuracy; and with the evidence on the nature and distribution of the nonhalide silver which is furnished by these analytical methods.

The methods used for the determination of silver liberated on exposure, in attempts (1)[1], (2) to verify the Einstein equivalence equation for photolysis of silver salts in photographic materials, are not sufficiently sensitive to detect nonhalide silver in unexposed emul-

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[1] Figures in parentheses here and throughout the text refer to bibliography at the end of the paper.

sions. By extrapolation of the data for silver formed on longer exposures, it has been estimated that photo-silver corresponding to normal image densities is of the order of 10^{-8} part of the total silver (3). The assumption that the sensitivity nuclei represent a fraction smaller, if anything, and quite beyond the reach of analysis, has been commonly made. The data of Sheppard (4) on sensitization by allyl thiocarbamide demonstrated that much higher proportions could be converted to silver sulphide at optimum conditions for sensitization, but there was no proof that all of this was necessarily effective. The analytical determination of nonhalide silver in unexposed developing-out emulsions was first announced by Weigert and Lühr (5). Their results showed a steady increase in the "Ursilber" of silver chloride and bromide emulsions during ripening, as is to be predicted if it is the product of this process. The amount of nonhalide silver was greatest in silver chloride emulsions, and least in those made with silver iodide; in the iodide emulsions it remained practically constant during ripening, in contrast to those made with the other halides. The absolute amounts of nonhalide silver were in all cases far above those for photo-silver corresponding to normal exposures.

In subsequent contributions (6), (7), (8) Weigert and Lühr have given full details of their methods and results. Their results have unfortunately been reported entirely in terms of weight of silver per unit plate area; as the results of other investigators have also been given in somewhat arbitrary terms, we have reduced everything to the common basis of the atomic ratio of nonhalide silver to the total silver in the emulsion. Weigert and Lühr's experimental emulsions were coated at 4.1×10^{-4} g equivalent AgBr per 100 cm^2 of plate; for commercial emulsions we have taken Eder's (9) average value of 9×10^{-4} for German plates. The Ag/AgBr ratio for commercial plates was approximately 2×10^{-4}; in experimental pure bromide emulsions it was 1.5 to 4×10^{-4} depending on the time of ripening.

Weigert and Lühr's procedure is based on the elimination of silver halide by fixing with sodium thiosulphate and washing, and analysis of the silver remaining in the emulsion film. The great increase in sensitivity over previous methods based on the same principle was obtained by differential electrometric titration of the silver with very dilute iodide solution. After fixing and washing, the emulsion film was scraped off the plate (9 by 12 cm) and boiled for five minutes with 0.8 ml of nitric acid, specific gravity 1.2, to break down the gelatin. The solution was then made up to 25 ml with the addition first of 1 ml of concentrated ammonia, next 0.5 ml glacial acetic acid, leaving it faintly acid. The prepared solution was divided between two crucibles, each provided with a silver electrode and a mechanical stirrer; the cell was completed by a salt bridge filled with agar jelly containing potassium nitrate. Potential differences between the electrodes were determined by connecting the cell directly to a highly sensitive galvanometer and reading the throw of the instrument after 30 seconds. The cell was short circuited between readings. In making the titration, iodide solution was added from separate burettes to each of the vessels, one being kept in excess by a small amount, usually 0.1 ml. Using 0.0001 *N* KI, the method was sensitive to 1×10^{-6} gram silver. Careful control determinations established that if the gelatin was broken down by the above procedure it caused no interference, and that the attack of the solution on the electrodes was negligible. Lühr noted that the first titration with the electrodes after they had been out of use for some time was generally low.

In the earlier part of their work, Weigert and Lühr simply fixed the plates in an alkaline thiosulphate bath[2] and washed thoroughly before stripping and analyzing. Experiments on plates coated with plain gelatin and bathed in fixing baths containing silver indicated that there was a blank of approximately 1×10^{-6} g equivalent of silver per g of gelatin, which could not be removed by washing after such treatment. They accordingly altered their procedure by the addition of a second fixing and washing after the first treatment; in view of the common practical use of double fixation to eliminate the last traces of silver salts from photographic materials, it is somewhat surprising that this had not been used in previous analytical methods depending on thiosulphate fixing. With this modification the blanks approached the limit of error of the titration. They lay considerable stress on thorough washing of the plates between the two fixing baths, reasoning that the removal of the silver held by the gelatin will be more complete as the ratio of sodium thiosulphate to silver thiosulphate is increased and that the optimum condition for use of the second bath is accordingly after the silver salts have been removed as far as possible by water. Their data show a decrease in the silver with increasing time of washing between the fixing baths. In some cases it reached an apparently constant value after washing for four hours, but more frequently there was an appreciable further decrease when the washing time was extended to five hours. In the case of ripened emulsions there is little room for doubt that there was a real quantity of silver much larger than the uncertainty of extrapolation to theoretically complete washing. A standard time of four hours was finally adopted.

Weigert and Lühr recognized that there is loss of silver during the fixing and washing processes since the solutions contain dissolved air, and any oxidation of the very finely divided metal will be followed by solution of the oxide in the thiosulphate. They tested the effect of from 2 to 10 successive fixing baths, 10 minutes each, on a ripened emulsion, the decrease in silver being very considerable with the larger numbers. The loss was less in 5 than in 20 per cent solution; after experiments with more dilute solutions, 5 per cent thiosulphate was adopted for the second fixing bath. We are unable, however, to find that Lühr determined the loss when plates containing known amounts of colloidal silver were given the standard treatment—10 minutes in alkaline 20 per cent thiosulphate, 4 hours washing in running tap water, 10 minutes in alkaline (?) 5 per cent thiosulphate and further washing. This was done with plates containing colloidal silver sulphide in quantities similar to the "Ursilber" of ripened emulsions; the loss, while probably real, was within the limits of error of the procedure.

It is obvious from the nature of the analytical procedure that the "Ursilber" would include both the silver sulphide and the metallic silver present in the emulsion. Weigert and Lühr came to the conclusion that it was almost entirely silver, because the "Ursilber" was greatly diminished by treatment with persulphate. In control

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[2] A reference to the work of Chapman Jones on the attack of fixing baths on the developed image indicates that the bath contained 200 g $Na_2S_2O_3.5H_2O$, 5 g Na_2SO_3, and 1 g Na_2CO_3 per liter, but we have been unable to find an explicit statement as to the amount of alkali.

experiments with colloidal silver sulphide in gelatin, persulphate failed to dissolve silver sulphide. These results are directly contradicted by Sheppard (10) in a recent communication in which he reports that known silver sulphide nuclei in emulsions were completely destroyed by persulphate. These emulsions were found also to contain silver in amounts somewhat smaller than the silver sulphide.

Weigert and Lühr's results have been attacked (11), (12), (13), principally because of the use of thiosulphate fixation, which other investigators had found to leave appreciable blanks depending on conditions such as the thickness of the emulsion film. These criticisms are answered by the use of the second fixing bath, in so far as they are based on the adsorption of silver thiosulphates by the gelatin. The very erratic results obtained by Arens and Eggert (12), using Weigert and Lühr's method, appear to reflect more on their experimental technique than on the method. Kieser (13) has pointed out that silver in the quantities reported ($Ag/AgBr = 1$ to 10×10^{-4}) might be detectable by its color; this also applies, however, to silver sulphide produced by sensitizers like allyl thiocarbamide, and it is not excluded that it actually would be visible by refined methods of comparison.

Shortly after Weigert and Lühr's first communication, Schmidt and Pretschner (14), working independently and by an entirely different method, reported the presence of excess silver in unexposed emulsions. Their values, reduced to the same basis, were about two or three times those obtained by Weigert and Lühr; for fast bromiodide emulsions, $Ag/AgBr = 8$ to 9×10^{-4} by one method, 2 to 3×10^{-4} by the other. Like Weigert and Lühr, they found that the amount of nonhalide silver increased with the solubility of the silver halide present in the emulsion and could not be correlated with the photographic properties of the emulsion. This apparent confirmation of Weigert and Lühr's results turned out to be accidental. Schmidt and Pretschner worked with large quantities of emulsion (about 0.7 kg) in the "noodles." The emulsion was thoroughly washed in tap water, followed by about 24 hours in changes of distilled water. It was then digested with nitric acid, 3 per cent of the total volume, which broke down the gelatin and coagulated the silver halide, and the silver in solution determined by very carefully corrected precipitation as silver chloride. Schmidt and Pretschner at first apparently considered that the silver determined in this way was present as metal. They later found (15) that on centrifuging emulsions the larger part of it remained in the gelatin, in contrast to photo-silver which was carried out with the silver halide of exposed emulsions. Further experiments (16), (17), (18) on sedimentation and on fixing silver chloride emulsions with sodium sulphite led them to the conclusion that most of the excess silver was not metal, but in some way combined with gelatin. Their final conclusion (19), (20), which we believe to be essentially correct, was that the excess silver was formed during washing by hydrolysis of the silver halide. They ascribed this, however, to the difference in rate of migration of the silver halide ions, which can not account for the results. The present authors in a preliminary note (21) have pointed out that the combination of silver ion with gelatin is responsible for this reaction; quantitative verification of this is given in our communication on the silver ion-gelatin equilibrium (22).

Sheppard (3) has recently reported the application of colorimetric determination of traces of sulphur compounds (23) to the determination of silver sulphide in the silver halide grains centrifuged from ripened emulsions. These results show the predicted increase in $Ag_2S/AgBr$ ratio with increasing specific surface of the grains (although it is noteworthy that the "medium" size grains have a distinct minimum, indicating that the "large" grains, first formed in the precipitation, reduced the concentration of labile sulphur compounds before the others were formed). They constitute an entirely independent confirmation of the existence of nonhalide silver in unexposed emulsions in the quantities first reported by Weigert and Lühr.

Our interest in the subject was primarily in connection with the determination of soluble bromide in emulsions. If there existed nonhalide silver in such quantities as were reported by Schmidt and Pretschner, this might well interfere with analysis for small amounts of bromides. Determination of nonhalide silver is also of use in any experiments on ripening and on nuclear sensitizers, although it is obvious from the available evidence (3) that the quantity is less important than its structure and relation to the silver halide grains. Being distinctly skeptical at first of the reality of the silver determined by any of the methods, we not only considered those published, but attempted independent verification by other processes which will be very briefly reported.

2. EXPERIMENTS WITH THE WEIGERT AND LÜHR METHOD

For the necessary electrometric titrations we used the apparatus which has already been described in another connection (22) measuring the emf of a cell consisting of the silver electrode in the solution to be titrated and a 0.1 N calomel electrode connected to it by a salt bridge filled with ammonium nitrate solution. While our procedure was not strictly a differential titration, the end point was always determined by a plot of $\Delta E/\Delta v$ against volume of solution. The procedure, involving the use of a potentiometer, is somewhat slower than that of Weigert and Lühr, but we found it a real advantage to be able to judge from the constancy of the potential whether the electrode was in equilibrium with the solution. Sluggishness which is completely negligible for the titration of 20 ml of 0.1 N solution is an entirely different matter when the end point comes at 1 ml of 0.00020 N KI. Like Clark (24) and Lühr (7), we found that the electrodes were more satisfactory after use; in fact, the first titration with dilute iodide solutions was quite unreliable. Unlike Lühr, we found it tended to be high rather than low; this is probably because the electrode after cleaning was usually made anode in dilute KI solution. All the experiments were made with 5 by 7 inch plates. Fixing and washing were carried on in new enameled trays, which were discarded when there was any indication of attack on the glaze, or in glass trays. In working with machine-coated experimental plates, the quantity of silver halide on the plate was determined by digesting the fixing baths with zinc. The resulting mixture of silver, silver sulphide, and excess zinc was dissolved in nitric acid and titrated with standard thiocyanate solution, using ferric alum as indicator.

We will, for convenience, refer to the quantity of silver halide per given area as the "coating thickness" of the plate; this quantity is, for a given emulsion, proportional to thickness although it is determined in terms of silver.

By presenting our results in an order quite different from that of the experiments we may develop the subject more logically and economize space. Table 1 gives the data for recent analyses of emulsions to which known amounts of colloidal silver and silver sulphide had been added. The reproducibility of the results for all but the controls was better than 5 per cent, and the values found agree with the amounts added within 12 per cent; in view of the uncertainty of measuring the volumes of emulsion used in making the knowns, the agreement with the true value may be better than this. The knowns were made by mixing the colloid with the emulsion just before coating, control batches being coated without such addition. The colloidal silver had been made by the dextrin method of Carey Lea as modified by Wiegel (25), and purified by two alcohol precipitations; the amounts given are corrected for the traces of silver salts present. Colloidal silver sulphide was prepared by adding first 2.34 ml of 0.107 *M* $Na_2S_2O_3$, then 5.0 ml of 0.100 *M* $AgNO_3$ to 170 ml of warm 1 per cent gelatin solution; the mixture was allowed to stand about an hour before use to complete the decomposition of the silver thiosulphate. The emulsions were not fully ripened, to keep down the nonhalide silver in the control; they were stabilized by adding 10 KBr per 1,000 AgBr before coating, and the analyses were made within two or three days after drying.

TABLE 1.—*Analysis by modified Weigert and Lühr method of emulsions containing known amounts of colloidal silver or silver sulphide*

Emulsion type	Colloid	Silver halide on 5 by 7 inch plate, gram equivalent $\times 10^4$	Nonhalide silver on 5 by 7 inch plate, gram equivalent $\times 10^7$	Ag/AgBr $\times 10^5$ found	Mean difference from control	Ag/AgBr $\times 10^5$ added
Ammonia process, pure bromide.	Control	13.2	0.96	7.3		0
		12.0	.52	4.3		
	Carey Lea silver	15.7	4.40	27.9	23.1	24.9
		17.5	5.24	29.9		
Neutral process, 3.4 mol per cent AgI.	Control	12.3	.48	4.2		0
		12.4	.56	4.5		
	Carey Lea silver	13.1	4.24	32.4	28.7	26.0
		12.3	4.16	33.8		
	Silver sulphide	13.7	4.88	35.6	30.4	34.5
		15.3	5.20	34.0		
	do	14.1	2.30	16.3	12.4	13.8
		13.7	2.36	17.2		

In these experiments we used a modification of the procedure recommended by Weigert and Lühr. The plates were first fixed for 10 minutes in a solution containing, per liter, 300 g $Na_2S_2O_3 \cdot 5H_2O$, 5 g Na_2SO_3 and 1 g Na_2CO_3; this was followed by two changes of a solution containing, per liter, 50 g $Na_2S_2O_3 \cdot 5H_2O$, 5 g Na_2SO_3, and 1 g Na_2CO_3, for five minutes each; the trays were rocked continuously during fixing, and all solutions were kept at less than 20° C. After fixing, the plates were washed for four hours in running tap water at 10° C., stripped, and titrated as already described.

This procedure was adopted in order to maintain at all times a high ratio of soluble thiosulphate to silver. Silver thiosulphate is very unstable unless this condition is fulfilled, and in our opinion the considerable positive errors found by Schmidt (26) and others in the analysis for nonhalide silver by a single fixation are caused more by precipitation of silver sulphide than by adsorption of silver compounds by gelatin. Kieser (27) has demonstrated that, on dissolving silver bromide in thiosulphate solutions after exposure to light, silver sulphide may be found in the residue. In some cases the results for silver may be high, indicating that in addition to conversion of the photolytic silver to sulphide, there may be a precipitation of silver sulphide on the former. Furthermore, our data (22) on the combination of silver ions with gelatin indicate that the amount of silver per gram of gelatin which was found by Weigert and Lühr after a single fixation corresponds at pH 7 to a silver ion concentration of $10^{-8}\,N$, which could hardly exist after four hours of washing. Adsorbed silver would at least be partly removed by extraction of the gelatin with acid, but when plates were fixed and washed by the original Weigert and Lühr procedure, then extracted three times with 0.005 $N\ H_2SO_4$ before stripping, no trace of silver could be found in the acid extract and the silver found in the stripped emulsion was not decreased.

Weigert and Lühr determined the blank on their procedure by coating plates with gelatin containing silver bromide dissolved in sodium thiosulphate. Blank emulsions for this purpose are somewhat difficult to prepare. Any emulsion in which silver nitrate solution has been even in momentary contact with gelatin may contain silver or silver sulphide. If the silver bromide is precipitated from aqueous solution with excess of bromide and then emulsified in gelatin, this objection is avoided, but the emulsion is liable to contain lumps which fix too slowly. The most satisfactory process is that originally suggested by Abegg and Hellwig (28), the silver bromide (plus iodide) being dissolved in a hot strong solution of a soluble bromide, and precipitated by diluting this with gelatin solution. The high concentration of soluble bromide liquefies the gelatin, so that we found it desirable to centrifuge the resulting emulsion and resuspend in fresh gelatin. The soluble bromide present was still much higher than normal so that the possibility of reaction of the silver halide with gelatin was minimized. Emulsions prepared by this procedure and coated in commercial thickness (15×10^{-4} g equivalent on a 5 by 7 inch plate) showed no nonhalide silver whatever in quadruplicate analyses by the modified method just described, demonstrating that the results with normal emulsions can not be ascribed to silver retained by the gelatin or to silver sulphide from decomposition of silver thiosulphate. It is necessary to specify, however, that the solutions and wash water be kept cool, and that the coating thickness shall not be excessive. Experiments with similar emulsions extracted by the original procedure and washed at higher temperatures (the tap water having been as warm as 30° C.) gave positive values for silver which increased with the temperature and time of washing.

Schmidt and Pretschner (26) reported that the nonhalide silver found after a single thiosulphate fixation and washing increased with increasing coating thickness of the plate. The original and modified Weigert and Lühr procedures were therefore tested for their dependence on this variable. The results are presented in Figures 1 and 2 by

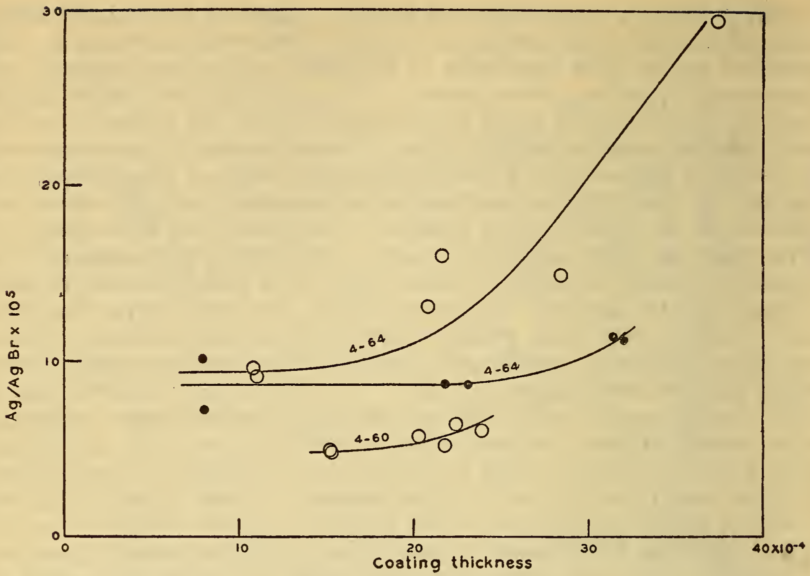

FIGURE 1.—*Variations in the results of determinations of nonhalide silver in plates with varying thickness of emulsion coating*

The data are for experimental emulsions 4–60 and 4–64
(.) Determinations by the original Weigert and Lühr method
(○) Determinations by the modified Weigert and Lühr method

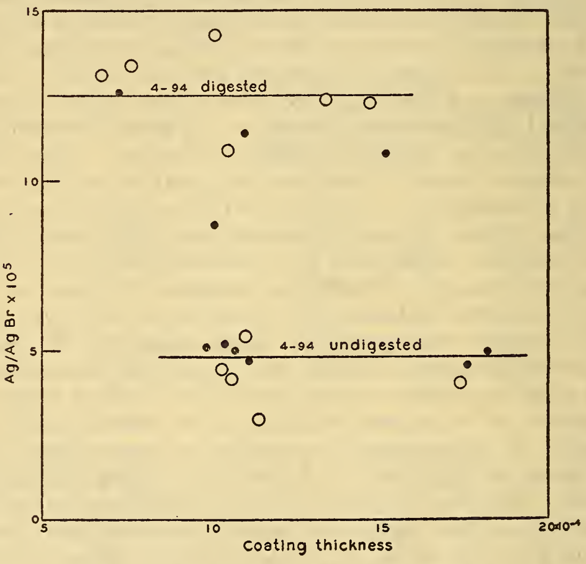

FIGURE 2.—*Variations in the results of determinations of nonhalide silver in plates with varying thickness of emulsion coating*

The data are for experimental emulsion 4–94.
(.) Determinations by the original Weigert and Lühr method
(○) Determinations by the modified Weigert and Lühr method
Note also the increase in nonhalide silver produced by digestion

plotting the nonhalide silver/silver halide ratio against the coating thickness (in terms of g equivalents of silver halide per 5 by 7 inch plate). If the results were independent of the coating thickness, the plot should be a horizontal straight line; an increase in the ratio indicates that the results are not independent of coating thickness. The scattering of the points about the curve also indicates the reproducibility of the methods. Three emulsions were analyzed by the original[3] procedure and four by the modified. Emulsion 4–94 (Fig. 2) was prepared especially for these tests; one-half was coated with the minimum of digestion after washing, the other after two hours, digestion at 55° C. Each half was coated at several thicknesses. The difference in nonhalide silver produced by digestion is obvious.

The reproducibility by the two procedures is about the same; random variations of ± 20 per cent were encountered in some cases. This is not quite as good as the results obtained by Lühr, but is of the order of the systematic errors of the method. The coating thickness did not affect the results up to a value of about 0.15 g AgBr per 100 cm^2 (18×10^{-4} g equivalent per 5 by 7 inch plate); this is the maximum which we have found on commercial emulsions. Thicker coatings, which were found on some of the experimental plates, introduce a positive error; the original procedure was the better of the two in this respect, but either one became unreliable.

Having established the order of accuracy and reproducibility of the analytical method, the next consideration is the evidence concerning the nature of the nonhalide silver in photographic emulsions which may be derived from further study.

It is interesting to find that the Weigert and Lühr procedure gives correct results for colloidal silver in an emulsion, even though the thiosulphate solutions, which are of course saturated with air, attack the same colloidal silver under other conditions. Some of our first tests of the method were made by adding colloidal silver to gelatin and coating on plates so that the gelatin and silver corresponded to the quantities of gelatin and nonhalide silver in emulsions. When these plates were put through the fixing baths and washing, the loss of silver was 30 to 90 per cent, being less for larger amounts of silver. This applied both for Carey Lea silver (the same sample used in the emulsions of Table 1) and for argyrol, losses in the latter case being corrected for the silver proteinate present. It has been suggested (27) that colloidal silver in the emulsion would be converted during fixing to silver sulphide. This would explain the failure of the fixing baths to attack colloidal silver when present in an emulsion, since, in agreement with Weigert and Lühr, we found that the attack on colloidal silver sulphide was small even when it was coated in plain gelatin.

Although the method may give correct results for colloidal silver present in emulsions, we can not agree with Weigert and Lühr that this is the main component of the nonhalide silver ("Ursilber"). We found, in agreement with Sheppard (10), that colloidal silver sulphide is attacked by persulphate. The data are given in Table 2. The silver sulphide was prepared by the decomposition of silver thiosulphate, as described on page 716, and diluted with 6 per cent gelatin solution to the desired concentrations before coating. It is evident

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[3] Except for the use of 300 g thiosulphate per liter.

from the data that this same sample was not seriously attacked by thiosulphate solutions. The persulphate solution was 0.10 N $(NH_4)_2S_2O_8$ and 0.10 N H_2SO_4, acting for one hour at 20°, without subsequent washing.

TABLE 2.—*Attack on colloidal silver sulphide by thiosulphate and by persulphate*

(All results expressed as gram equivalents of silver × 10^7 per 5 by 7 inch plate)

Original amount	Residue	
	After modified Weigert and Lühr treatment	After persulphate treatment
4. 26, 4. 24	3. 04, 3. 24	1. 3, 1. 0
9. 76, 9. 76	9. 74, 9. 26	1. 14, 1. 74

The quantity of nonhalide silver found in emulsions has been one of the principal objections to its identification with the sensitivity nuclei. Even unripened and insensitive emulsions contain amounts much larger than is necessary ((29), Tables 29, 30, 31) under favorable conditions to multiply their sensitivity manyfold. We accordingly suggested the hypothesis that most of the nonhalide silver had been formed by reactions involving silver ions or silver-gelatin complexes, while the sensitivity nuclei were formed by rearrangement of compounds first adsorbed to the grains. We have since realized that this may be tested experimentally, as the two classes can be separated by centrifuging the emulsion, and determined by analyzing the silver halide grains and the cleared gelatin. Three emulsions were made up for this purpose. Portions of each were coated unchanged. The rest of the emulsion was separated in the centrifuge, and the cleared gelatin coated in the same way, at about the same thickness, as the original emulsion. In two cases the separated silver halide was again emulsified in fresh gelatin and coated like the rest. The plates were analyzed by the modified method; the coating thickness was excessive, but there are no indications of difficulty from this source. The data in Table 3 clearly demonstrate that the nonhalide silver is associated with the grains and not dispersed through the gelatin. The data given by Sheppard (3) for the silver sulphide in emulsion grains, obtained by a different analytical method, are obviously proof of the same point. The explanation of the existence in the same emulsion of silver sulphide of widely varying effectiveness in sensitizing remains to be provided. It is obvious that some other function of the silver sulphide is overwhelmingly more important than its total quantity.

TABLE 3.—*Distribution in emulsions of nonhalide silver determined by the Weigert and Lühr method*

Type of emulsion	Coating on plate	Total silver on plate, gram equivalents $\times 10^4$	Nonhalide silver on plate, gram equivalents $\times 10^7$	Ag/AgBr $\times 10^5$
Neutral, pure bromide	Original emulsion	22.6	1.88	8.3
		21.8	1.42	6.5
	Cleared gelatin	.1	.4	----------
		.1	.3	----------
	Silver bromide in fresh gelatin	23.6	2.24	9.5
		24.0	2.12	8.9
Ammonia ripened, 1 per cent AgI	Original emulsion	17.3	4.80	27.7
		15.8	4.34	27.4
	Cleared gelatin	.2	0	----------
		.2	0	----------
	Silver halide in fresh gelatin	21.6	7.5	34.7
		21.1	6.16	29.2
	Original emulsion	34.2	2.78	8.1
		33.5	2.68	8.0
	Cleared gelatin	.3	0	----------
		.3	0	----------

3. EXPERIMENTS WITH OTHER METHODS

(a) DIRECT EXTRACTION WITH NITRIC ACID

Direct extraction with nitric acid as recommended by Schmidt and Pretschner, dissolves silver in every form likely to be present except the halides. Soluble halides must be completely removed or they will react with the dissolved silver. The extensive washing necessary to remove the halides results in the formation of silver-gelatin compounds if the washing is done with pure water, with consequent positive errors many times the quantities to be determined. As Schmidt and Pretschner have recognized this, it will be unnecessary to present all the data accumulated to prove the point.

The apparatus for electrometric titration being available, we substituted this for the gravimetric methods of Schmidt and Pretschner, and worked with the emulsion from a 5 by 7 inch plate instead of with larger quantities as "noodles." The sensitivity of the titrations was less than those for the Weigert and Lühr method; the final solution being saturated with silver bromide, it is necessary to titrate with bromide solution and the end point is less sharp because of the greater solubility of silver bromide. The uncertainty of a titration was about 2×10^{-7} g equivalent of silver, as against 0.4×10^{-7} with iodide. The coating thickness of the plates was readily determined by an application of the Liebig method for cyanides. The coagulated silver bromide was filtered off after the nitric-acid digestion, and dissolved in standard sodium cyanide solution. The excess cyanide was then titrated with silver nitrate solution, using the appearance of turbidity as the end point.

The principal systematic error in the determination of nonhalide silver in emulsions by nitric-acid extraction is caused by the formation of silver-gelatin compounds while extracting soluble bromide. This may be eliminated by extracting the bromide with dilute acid instead of with water, as will be explained in more detail in the second part of this paper. However, the sensitivity of the method is insufficient. The changes in nonhalide silver produced by after-ripening could be detected, but were little larger than the uncertainty of the titration.

Nitric acid extraction was used in the determination of silver-gelatin compounds in emulsions; these results will be given in the second part of this paper.

(b) CYANIDE FIXATION

If an unexposed and undeveloped plate is fixed in a cyanide solution under ordinary conditions, followed by adequate washing, all silver will be removed; even silver sulphide will be dissolved by complex ion formation, and small amounts of finely divided silver will be attacked by the dissolved oxygen in the solution and then dissolved by the cyanide. If oxygen were quantitatively removed from the solutions, it might be possible to fix with cyanide, thus removing silver halide and sulphide, and to determine the remaining metallic silver. An apparatus was built in which it was possible to free a liter of water from dissolved gases by refluxing in vacuum for several hours; portions of this water were then transferred to a tube containing the strip of plate to be analyzed, and solid sodium cyanide. The cyanide solution thus prepared in the absence of oxygen fixed the plate and was replaced by successive portions of water. The whole apparatus could be rocked to insure agitation. The attack on silver was tested by using a strip of plate coated with colloidal silver (free from silver salts) in gelatin, 3.3×10^{-6} g equivalent Ag. Using single fixation followed by four changes of water, no silver could be detected in the acidified extract from one run; in a second run where some leakage of air into the apparatus had occurred 3×10^{-7} g equivalent of silver was found in the extract. Complete removal of silver from the emulsion was found to require more thorough washing. Test strips of Eastman 33 plates were fixed in the apparatus in two changes of cyanide solution (a second portion of the solid salt being held out of contact with the solution during the first fixation), followed by six changes of water. No silver could be detected in the remaining emulsion. The method was abandoned at this point as too cumbersome and uncertain.

If the emulsion is freed from soluble bromide and then fixed in air, all silver is extracted, provided the amount present as metal is small. If the fixing bath was then acidified and evaporated to remove hydrocyanic acid (using a hood for this operation), it was found by experiment that silver sulphide and silver halides were precipitated quantitatively, but that traces of silver originally present as metal remained in solution. Apparently if silver cyanide was first precipitated, it was decomposed during the evaporation if the quantity was small enough. This method was of possible interest, since it might be a means of determining metallic silver but not silver sulphide. However, it is obviously dependent on removal of soluble bromide, and any silver-gelatin compounds formed in this process appear in solution and can not be distinguished from metallic silver. Attempts to apply the process to the determination of soluble bromide will be reported in the second part of this paper.

Other solvents were also considered. Sulphite unfortunately can be used only for chloride emulsions. Ammonia was reported by Schmidt (17) to give "very disturbing side reactions"; the nature of these will be discussed in a separate communication on hypersensitization by ammonia solutions.

It is possible that the nonhalide silver might be determined in the emulsion after extraction with acid solutions of thiocarbamides, or with thiocyanates, but neither of these methods were tested.

II. DETERMINATION OF SOLUBLE BROMIDE

The determination of soluble bromide in photographic emulsions is of considerable practical interest because of the effect of this constituent on the ripening and after-ripening process, the sensitivity (especially in the presence of sensitizing dyes) and the stability on storage. The analytical problem appears superficially to be very simple, and probably for this reason has received very little mention in the literature.

Since the soluble bromide is at most about 1 per cent of the total bromide, it is obvious that it can be more accurately determined if separated from the silver bromide. The extraction of the soluble bromide from the emulsion is subject to an unexpected positive error from the formation of silver-gelatin complex and consequent decomposition of silver bromide, which leads to high results. The combination of silver ion with gelatin has been quantitatively studied in this laboratory (22). Its existence was independently inferred by Mitchel and Rawling (30). They analyzed emulsions of known composition by coagulating the gelatin and silver bromide and determining soluble bromide in the filtrate. The results were high in bromide by an amount increasing as the excess of bromide over silver was decreased. Chloride emulsions gave a larger error in the same direction, while iodide emulsions were slightly low in iodide recovered, indicating adsorption. Their data are quite consistent with the formation of silver-gelatin complexes in amounts increasing with the silver ion concentration of the emulsions. If the error from this source is eliminated, the remaining problems are the completeness of extraction of the soluble bromide and its determination in small quantities such as are obtained from reasonable areas of photographic materials.

The methods here proposed are based on the use of acid to prevent the formation of silver-gelatin complexes. Electrometric titration has been used in most of the experiments for the determination of soluble bromide in the extracts, and is strongly recommended for this purpose. The acid extracts may, however, be analyzed by other methods.

As the combination of silver ion with gelatin (22) failed to disappear completely at any hydrogen ion concentration which was tested, the conditions under which it became negligible during extraction of bromide from plates were tested directly. Table 4 gives the data for the extraction of commercial plates (Eastman 33) with varying concentrations of acid. Five by seven inch plates were used in the experiments, the emulsion on each plate containing $15.4 \pm 0.4 \times 10^{-4}$ g equivalent of silver halide. Three extractions were made with 100 ml portions of acid, rocking the plate for three minutes in each. After the extractions, the emulsion was stripped off and analyzed for nonhalide silver by digestion with 0.5 *N* HNO_3.

Results are given in terms of the ratio of equivalents of soluble bromide or nonhalide silver per equivalent of silver halide.

TABLE 4.—*Extraction of soluble bromide from Eastman 33 plates, and nonhalide silver in plates after extraction*

Solvent used for extraction	$Br^-/AgBr \times 10^3$	Nonhalide silver, after extraction $Ag/AgBr \times 10^3$	Solvent used for extraction	$Br^-/AgBr \times 10^3$	Nonhalide silver, after extraction $Ag/AgBr \times 10^3$
Water	3.0	[1] 1.47	0.0050 *N* H_2SO_4	2.03	0.29
	2.9	[1] 1.44			.26
	3.7	[1] 1.46	0.025 *N* H_2SO_4	2.03	.30
	3.7	[1] 1.46		2.00	.25
			0.125 *N* H_2SO_4	2.05	.23
0.010 *N* [2] acetic acid	2.06	.45		1.99	.25
	2.10	.43	Chrome alum 10 g/liter	2.02	
0.0010 *N* H^2SO^4	3.80	.51		2.06	.22
	3.80	.45		2.06	.25
	2.24	[1] .29		1.97	.25
	2.31	[1] .29			

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[1] Determined by direct electrometric titration of acidified stripped emulsion, instead of nitric acid extraction.

[2] Five extractions.

This procedure was found to give complete extraction within the limits of error of the titration of the extracts. For example, successive extracts of the Eastman 33 plates with water were found to be equivalent to the following, in ml of 0.0010 *N* $AgNO_3$: First, 4.18, 4.0; second, 0.5, 0.5; third, 0.0, 0.0. Using 0.010 *N* HAc, the combined first extracts from two plates were equivalent to 5.8 ml; the second to 0.51 ml, and the third, fourth, and fifth each to 0.0.

The data on bromide extracted and on nonhalide silver remaining show that a constant minimum is reached with solutions as acid as 0.005 *N* H_2SO_4 (pH approximately 2.7). The nonhalide silver remaining after extraction with the more acid solutions represents silver sulphide rather than silver-gelatin complex, since it checks the nonhalide silver in these same plates found by the Weigert and Lühr method (mean value 0.21×10^{-3}) which includes only silver and silver sulphide.

The chrome alum solution was tested because it seemed likely to be useful for extracting emulsions with a tendency to loosening from the base; electrometric titration may be made without eliminating the alum, although $\Delta E/ \Delta v$ at the end point is smaller. The pH of chrome alum solution, 20 g/liter, is 2.16 by the quinhydrone electrode.

The extraction with chrome alum solution (10 g/liter) was tested on an experimental emulsion to which soluble bromide had been added after a thorough washing. 8.0 ml of 0.111 *N* KBr had been mixed with half the emulsion, containing 0.16 g equivalent silver halide, giving a ratio $Br^-/AgBr$ of 5.5×10^{-3}. Extractions of plates from the half without added bromide contained 0.0, 0.0, 0.0, 0.1×10^{-3} $Br^-/AgBr$; from the half with bromide the ratios were 5.35, 5.33, 5.56, 5.41×10^{-3}. The difference is within the limits of error in making up the known.

While the above data indicate that relative amounts of soluble bromide in different portions of the same emulsion may be determined by extraction, there remained the possibility that the silver halide grains may carry appreciable amounts of alkali bromide which is irreversibly adsorbed or even in solid solution, and hence not to be removed by such extraction. This could be liberated by fixing the plate. Accordingly, the whole emulsion of Eastman 33 plates was analyzed by the method of Clark (24). After fixing in two changes of cyanide solution, followed by two changes of distilled water, the silver was reduced by digesting with zinc. The halide solution was filtered and hydrocyanic acid eliminated by boiling with acetic acid. The silver and zinc were dissolved in nitric acid and excess nitric acid driven off by gentle heating. The silver nitrate plus zinc nitrate was then dissolved and the silver and halide solutions made up to known volumes and titrated against each other electrometrically. The ratio Ag: halide thus obtained was 1.004, 1.004, 1.002:1. The error in this method is obviously of the same order of magnitude as the soluble bromide present. It indicates, however, that the adsorbed bromide left after extraction with the dilute acid can not be large.

Repeated attempts were made to determine total soluble bromide, including possible adsorbed material, by a modification of this process. The plates were fixed in 1 per cent NaCN, followed by 0.1 per cent NaCN and two changes of water. Hydrocyanic acid and dissolved silver salts were eliminated by acidifying with sulphuric acid (double the amount necessary to liberate the hydrocyanic acid) and twice evaporating to half volume on the steam bath, after which the solution was filtered and titrated electrometrically. Starting with known amounts of silver nitrate and potassium bromide, the correct value for excess bromide was obtained by this procedure. However, the results with extracts from plates were erratic; and the electrode potentials were unsteady unless the solution were strongly acidified during titration. It was found that extracts from certain samples of gelatin produced very similar results when added to controls, indicating reduction of silver bromide by the combined action of the cyanide and organic extract from the gelatin. It is interesting that other samples of gelatin caused no such trouble. Mitchel and Rawling were able to determine bromide in the presence of gelatin by the Lang method (31), which is based on oxidation of the bromine to cyanogen bromide and titration of iodine liberated by the cyanogen bromide after first removing the excess of oxidizing agent. This method was therefore applied to the solutions from the cyanide fixation. The apparent errors were not as large as those of electrometric titration of these solutions, but the results were not satisfactory by either method.

The Volhard method obviously might be used for the determination of bromide in the extracts if chloride were known to be absent, but this will seldom be the case. The adsorption indicators, such as fluorescein, can not be used for titration of halide against silver in the presence of protective colloids, such as gelatin extracts.

As the Lang method was found by Mitchel and Rawling (30) to work in the presence of gelatin, it was tested for use on the acid extracts from emulsions. The plates were extracted three times with 0.005 N H_2SO_4 and the combined extracts neutralized with Na_2CO_3 and evaporated to about 10 ml. One to three ml of sirupy phosphoric acid, 3 ml N $KMnO_4$ and 3 ml 0.5 N NaCN were rapidly added to each sample, and the flasks stoppered and left to stand for 20 minutes; no loss was caused by increasing the time to 30 minutes. After the oxidation was complete, the excess $KMnO_4$ and MnO_2 were eliminated by adding saturated $FeSO_4$ solution in slight excess, followed by about 1 g solid KI. After a minute the liberated iodine was titrated with 0.001 N $Na_2S_2O_3$ solution with starch as indicator.

It seems worth reminding the chemist who has not previously used the Lang method that the final reaction is as follows:

$$BrCN + 2H^{\cdot} + 2I^{-} = HCN + 2I + H^{\cdot} + Br^{-}$$

In the presence of organic matter, such as gelatin or gelatin extracts, we found it necessary to increase the amounts of $KMnO_4$ and NaCN and the time of oxidation as indicated, even though Mitchell and Rawling report satisfactory results with 1 ml N $KMnO_4$ and 0.5 ml of 0.5 N NaCN, the proportions recommended by Lang. Examples are given in Table 5. Results, were slightly low in all cases and unless there is a distinct excess of $KMnO_4$ at the end of the oxidation and sufficient cyanide to insure that the Br goes quantitatively to BrCN, the error is very serious.

Comparison of the Lang and electrometric titrations of extracts from plates is given in Table 6. Values obtained by the Lang method were in all but one case lower than those found by electrometric titration. Interfering material of unknown character apparently was responsible for a loss of over 20 per cent in the determination of bromide from the second emulsion by the Lang method. Results with the other emulsions may be described as tolerable for practical use.

TABLE 5.—*Determinations by Lang method of 10.0 ml of 0.00100 N* KBr *to which was added either 1 g gelatin, or acid extracts from 1 g gelatin*

(Calculated volume of 0.0011 N $Na_2S_2O_3$, 18.2 ml)

Added material	N $KMnO_4$	0.5 N NaCN	Time of oxidation	0.0011 N $Na_2S_2O_3$
	ml	*ml*	*Minutes*	*ml*
Gelatin	2.0	0.5	5	11.7
				12.4
	5.0	.5	5	8.0
			+	14.5
	5.0	5.0	5	15.1
			10	15.1
			15	16.5
			25	17.2
Extract	1.0	.5	5	10.8
			5+	11.1
	5.0	5.0	20	17.0
			28	17.6
			35	17.3
			40	17.3

TABLE 6.—*Analysis of extracts from plates (with 0.005 N* H_2SO_4*) by electrometric titration and by Lang method*

Emulsion	$Br^-/AgBr \times 10^3$	
	Electrometric titration	Lang method
Commercial unsensitized No. 1	1.90, 1.93, 1.93	1.91, 2.01.
Commercial unsensitized No. 2	8.99, 8.90, 8.70, 8.79	6.8, 6.8.
Commercial panchromatic	0.96	0.84, 0.84.
Experimental 10–2	7.92, 7.99	7.2, 7.4.

In the case of emulsions before coating, we have found that the direct determination of bromide ion concentration by the silver-silver bromide electrode, using only the potential of the electrode in the emulsion without a titration, is quite satisfactory for control of washing, digesting, and coating conditions, and is very readily carried out if the apparatus is available. It is also possible to determine the amount of soluble bromide by acidifying the emulsion to pH 2 (approximate) and making an electrometric titration; the normality so obtained will not agree with the concentration of free bromide ions found by the electrode potential because of adsorption, and the combination of silver ions with gelatin. The accuracy of the titration may be illustrated by the figures for emulsion 10–2. This was washed thoroughly, then melted and mixed with KBr solution making it 0.00097 *N*. Electrometric titrations gave 0.000965, 0.00098, 0.00097 *N*. The concentration of the emulsion was by mistake not accurately determined but these titrations correspond to about 7.5×10^{-5} Br/AgBr, as compared to 7.9×10^{-5} by extraction of the finished plates. (Table 6.)

Mitchel and Rawling's method for determination of bromide in the emulsion before coating is based on coagulation of the emulsion by magnesium sulphate and alcohol. The error resulting from the combination of silver ion with gelatin might be eliminated if the emulsion were sufficiently acid when coagulated, but we were unable to secure a satisfactory coagulation at pH 2. The electrometric methods only can be recommended for the liquid emulsion, on the basis of our experience.

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