

CIV.—*The Electrometric Titration of Halides.*

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THE object of the experiments to be described was to examine the possibility of applying electrometric methods to the analysis of mixtures of soluble halides and of mixed silver halides, in particular where one halide is present in small proportion—less than 1%—in the other.

The estimation of a single soluble halide by titration with silver nitrate, or conversely of silver ions by titration with a halide solution, can be accurately and simply carried out electrometrically (compare Behrend, *Z. physikal. Chem.*, 1893, **11**, 466; Dutoit and von Weise, *J. Chim. Phys.*, 1911, **9**, 578, 608, 630). For this purpose several different methods have been devised. Certain of these have been summarised by Kolthoff (*Chem. Weekblad*, 1920, **17**, 659), Willard and Fenwick (*J. Amer. Chem. Soc.*, 1922, **44**, 2504), and Müller (“*Elektrometrische Massanalyse*,” 2nd edn, 1923).

The most exact method of titration is that in which the titration beaker containing the halide solution and a silver electrode is

connected with a normal electrode, and the *E.M.F.* of the combination is measured after each addition of silver nitrate, the end-point of the titration being taken as the point of maximum rate of change of *E.M.F.* with silver ion added.

In an arrangement due to Pinkhof (*Diss.*, Amsterdam, 1919; *Chem. Weekblad*, 1919, **16**, 1163; *Pharm. Weekblad*, 1919, **56**, 1218) the normal electrode is replaced by a compensation electrode whose potential is equal to that of the titration system at the end-point. With this method a different compensation electrode would be required for each halide titrated, and in the titration of mixed halides the electrode would have to be changed during the course of the titration.

A variation of Pinkhof's method has been used extensively by Treadwell (*Helv. Chim. Acta*, 1919, **2**, 672, 680), and a modification for use with 5 c.c. of solution to be titrated, has been described by Garner and Waters (*J. Soc. Chem. Ind.*, 1922, **41**, 337T).

A further method of titration consists in the use of "bimetallic electrode systems," introduced by Willard and Fenwick (*J. Amer. Chem. Soc.*, 1922, **44**, 2504, 2516; 1923, **45**, 623), and suggested also by Müller (*Z. Elektrochem.*, 1924, **30**, 420) and Hostetter and Roberts (*J. Amer. Chem. Soc.*, 1919, **41**, 1343). This method has been applied also to acid-alkali titrations by van der Meulen and Wilcoxon (*Ind. Eng. Chem.*, 1923, **15**, 62) and by Brünnich (*ibid.*, 1925, **17**, 631).

Another method of titrating soluble halides has recently been described and is worthy of note. In the "differential titration" method of Cox (*J. Amer. Chem. Soc.*, 1925, **47**, 2138) the halide solution is divided equally between two beakers joined by an ammonium nitrate bridge and each containing a silver electrode connected with the potentiometer. Both solutions are titrated simultaneously with silver nitrate, one being kept slightly in advance of the other, and the potential is read after each addition of silver. The titration curve obtained is the first derivative of the normal titration curve, and its maximum is the end-point.

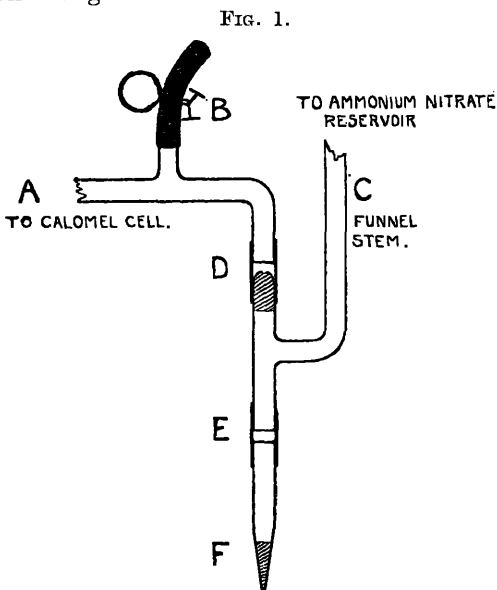
In the investigation to be described the first method of titration was used, *i.e.*, that in which the solution to be titrated contained a silver electrode and was united with a calomel cell, the *E.M.F.* of the combination being measured by means of a potentiometer after each addition of silver nitrate. This method was used because it is quite straightforward and can be used for the titration of mixed halides without changing the electrode or the constant half-cell. It was examined first with a view to its utility for the accurate yet simple estimation of mixtures of two or three alkali halides by direct titration with silver nitrate solution, and then for estimating

mixtures of silver halides. In a few instances, other methods of titration were tested.

### EXPERIMENTAL.

The calomel cell employed was of the saturated potassium chloride type. This was united with the halogen solution to be titrated by a saturated ammonium nitrate bridge in such a way as to prevent diffusion of chloride from the cell into the titration beaker, and to prevent loss of halide from the solution to be titrated by displacement with the specifically heavier ammonium nitrate solution. The arrangement is shown in Fig. 1.

A is a continuation of the side arm of the calomel cell. In the cell itself a wad of glass wool is placed over the surface of the calomel to prevent its disturbance when flushing out with fresh potassium chloride solution. At B is a side tube with clip to allow of the easy removal of air or old potassium chloride from the tube A D when filling it or when renewing the potassium chloride solution. An ordinary separating funnel is used as a reservoir for the saturated ammonium nitrate.



The end of its stem, C, is bent at right angles and a T-piece, D E, is joined on so that D E is parallel to the stem of the funnel. At the upper end, D, the T-piece is constricted, leaving an orifice about 1 mm. in diameter. This partially closed end D is packed tightly to a depth of 1 cm. with filter-paper, previously moistened with ammonium nitrate solution. The lower end, E, of the T-piece is joined by rubber tubing to a drawn-out tube, F, which is immersed in the solution to be titrated. The tapered end of F is also packed tightly to a depth of 1 cm. with a wad of filter-paper moistened with ammonium nitrate solution. The calomel cell is connected with the ammonium nitrate bridge at D by a short piece of rubber tubing.

By means of the side tube and clip at B it is possible to flush out the calomel cell with fresh potassium chloride solution without disturbing the ammonium nitrate bridge. By removing the tube F the nitrate bridge can be flushed out from the reservoir above without disturbing the calomel cell. It is not necessary to change the wad of filter-paper at D often, but the tube F should be changed frequently.

Observations showed that in the course of several hours no chloride reached the titration solution from the calomel cell, and no loss of chloride from the titration solution into the bridge could be detected.

The solution to be titrated was stirred by a motor-driven stirrer at 200 revolutions per minute.

For the silver electrode, No. 20 gauge fine silver wire, provided by Messrs. Johnson Matthey, was used. For the best results it has to be specially treated, as described later. A Cambridge and Paul potentiometer, giving readings to 0.5 millivolt, was used for measuring electromotive forces.

The method of titration was to run standard silver nitrate solution *drop by drop* into the stirred solution of halide, the *E.M.F.* being read after each addition of 1 c.c. When the *E.M.F.* began to rise more rapidly, only 0.1 c.c. of silver nitrate solution was added. When great accuracy was desired, or when only small amounts of halide were being titrated, silver nitrate was added from a micro-burette, or more generally, a *N/100*- or *N/1000*-solution was used, in the neighbourhood of the end-point.

In most cases, a certain time was necessary for establishment of equilibrium of *E.M.F.* in the immediate neighbourhood of the end-point. This will be considered in the course of the description of the titration. The end-point of the titration was obtained either by plotting the titration curve of c.c. of silver nitrate added against *E.M.F.*, and determining its point of inflexion or the mid-point of the maximum slope, or, more readily, by plotting the first derivative of the titration curve, *i.e.*,  $dE/dV$ , against *V*, where *E* is the *E.M.F.* corresponding to a volume *V* of silver nitrate added (compare, for example, Hostetter and Roberts, *J. Amer. Chem. Soc.*, 1919, **41**, 1341). Each of these methods of determining the end-point was used as occasion demanded, for in certain forms of titration curve one method is preferable to another.

#### *Titration of Solutions of Soluble Halides.*

*Preparation of Pure Materials.*—Silver nitrate solutions of *N/10*, *N/100* and *N/1000* strength were made up from Johnson's "pure

triple crystallised silver nitrate," which is specially prepared for the manufacture of photographic emulsions.

Potassium chloride, free from other halides, was available as a commercial product, and approximately *N*/10-solutions were prepared.

No commercial sample of bromide or iodide free from chloride was available. Many samples of ammonium and potassium bromide, and of ammonium, barium, cadmium, and potassium iodide were examined quantitatively for chlorides. The proportion present varied with different samples from 0.2% to about 5%, and with a number of samples of any one salt from any one manufacturer, wide variations were found. Potassium bromide was the worst offender in this respect.

*Preparation of Pure Bromide.*—A sample of potassium bromide, free from chloride and bromate, was prepared by heating once-recrystallised potassium bromate in a silica basin, extracting the fused salt with water, and evaporating the solution to dryness.

Ammonium bromide free from chloride was prepared from purified ammonia and bromine. A sample of commercial ammonia solution, labelled "sp. gr. 0.880, extra pure," contained a trace of chloride which was removed by boiling off the ammonia gas and reabsorbing it in distilled water.\*

For the preparation of pure bromine, the purest commercial bromine, which contained some chlorine, was used. 100 G. were shaken with 50 c.c. of concentrated potassium bromide solution, and then distilled off on a water-bath at 70—90°. The distilling apparatus was made entirely of glass, and the receiver was cooled in ice.

The yield of 70 g. of bromine was well shaken with 5 c.c. of *N*-caustic soda solution and distilled again in the same apparatus (compare Scott, J., 1913, 103, 847; Baxter, *Proc. Amer. Acad. Arts Sci.*, 1906, 42, 201).

Ammonium bromide was made by adding the bromine drop by drop, shaking after each addition, to freshly-distilled ammonia contained in an ice-cooled flask until there was only a slight excess of ammonia. This excess was boiled off and the solution evaporated to dryness. The product was free from chloride and bromate.

*Preparation of Pure Iodide.*—Baxter (*Proc. Amer. Acad. Arts Sci.*, 1903, 39, 249; 1904, 40, 419; 1906, 42, 201) has described the conditions for the preparation of pure bromine and iodine. The method he adopted in the case of iodine did not give successful results in the author's hands. Also attempts were made to prepare

\* Addition of a few drops of silver nitrate solution to the ammonia before distillation ensures the freedom of the final product from chloride.

pure ammonium iodide somewhat on the lines described by Baxter, but without success. It was found impossible to remove the last traces of chloride; under the conditions employed, between 0.1% and 0.2% chloride remained.

Some of the earlier experiments on electrometric titrations, to be described later, suggested a method for the preparation of iodide free from chloride which was very satisfactory and simple. It is briefly as follows :

Ordinary commercial potassium iodide is dissolved in a 5% solution of chloride-free barium nitrate (sodium nitrate, ammonium nitrate or sodium acetate may also be used) and silver nitrate solution is run in slowly drop by drop, with vigorous stirring, a marked excess of soluble halide, however, being left finally. This excess must be larger than the equivalent of chloride present. Silver equivalent to 90% of the iodide was used in the actual preparations. Under these conditions, the precipitate consists entirely of silver iodide and all the chloride remains in solution. The silver iodide precipitate is removed and washed several times with water. It is then suspended in water, stirred vigorously, and reduced with hydroxylamine sulphate\* and chloride-free caustic soda prepared from metallic sodium by the action of water vapour. This gives a precipitate of spongy silver, and a solution of sodium iodide, hydroxylamine, sodium hydroxide, and sodium sulphate. The liquid is filtered, evaporated to dryness, the residue is heated at about 200° to destroy the excess of hydroxylamine,† and extracted with water, and the solution neutralised with sulphuric acid. The solution of sodium iodide and sodium sulphate obtained in this way was suitable for the purpose of electrometric titration; in fact, the presence of sodium sulphate was found to be beneficial to the titration. The solutions obtained were absolutely free from chloride.

If it is desired to have pure iodide, free from sodium sulphate, the solution can be treated with permanganate, and the iodine distilled off and converted into hydriodic acid with hydrogen sulphide gas according to the method of Baxter (*loc. cit.*).

If the product still contains chloride, the iodide-sulphate solution can be again partly precipitated as silver iodide, followed by reduction as described, but in no case has more than one precipitation and reduction been found necessary.

Stock solutions of bromide and iodide of practically *N/10*-strength were prepared, and standardised against the stock *N/10*-silver nitrate solution, by the dye-indicator method of Fajans

\* This can be obtained commercially quite free from chloride.

† Alternatively, an excess of silver iodide is used so that there is no excess of hydroxylamine.

and Hassel (*Z. Elektrochem.*, 1923, **29**, 495; *Kolloid Z.*, 1924, **34**, 304), fluorescein being used as indicator. The stock chloride solution was standardised by the normal titration method, with chromate as indicator.

In the titration of silver ions with halide ions, with fluorescein as indicator, it is essential to define the conditions rather closely, otherwise the true end-point is difficult to determine. It is necessary to titrate in very dilute solution, with a low concentration of dye. For example, in the titration of *N*/10-silver nitrate with *N*/10-potassium bromide it was found best to dilute 10 c.c. of the silver nitrate to about 200 c.c. with water, and use 5 drops of a 1 : 2000 solution of fluorescein as indicator. In these conditions, the silver halide does not coagulate in the neighbourhood of the end-point, and the change from rose colour to yellowish-green is sharp and readily located.

#### *Electrometric Titration of Halides.*

The solutions of soluble halides were titrated electrometrically with a standard silver nitrate solution, and the results agreed identically with those obtained by the ordinary titrations. For any further stock solutions prepared, standardisation was therefore carried out by the electrometric method.

In the titration of the single halide solutions with silver nitrate, the magnitude of the potential jumps about the end-point was roughly : for chloride, 180 mv. ; for bromide, 350 mv. ; for iodide, 500 mv., being bigger the lower the solubility of the corresponding silver salt.

The procedure in titration was to dilute the volume of halide taken to 50 c.c. in some cases, or to 150 c.c. in other cases, with water or any required solution, and then to titrate with the *N*/10-silver nitrate.

In the titration of bromide or iodide, no anomalies were observed which could be ascribed to the nature of the silver electrode employed. In the case of chlorides, however, certain peculiarities were observed which were shown to be dependent on the electrode surface.

#### *Effects Due to the Electrode.*

The first electrodes used were cleaned by scraping with emery cloth or a knife blade. In the titration of chlorides, the addition of the first drop of silver nitrate resulted in a sudden rise in potential. This jump was by no means constant, being about 40—50 mv. in certain cases, and less than 10 mv. in others. With a higher concentration of chloride, a bigger jump was sometimes observed, and its magnitude was dependent to some extent on the presence of

neutral salts. Carrying out the titration in red light did not improve matters. The jump was not due to the presence of a trace of bromide or iodide in the chloride, since its magnitude was variable for the same amount of chloride used, but was due to some peculiarity of the silver electrode, since it varied with the nature of the silver surface.

To avoid any confusion in the event of the possibility of the presence of a trace of iodide or bromide in the chloride, the conditions for obtaining an electrode which did not give the initial jump were studied. A long series of experiments showed that plating the electrode from a potassium argentocyanide solution does not give a reproducible electrode which comes into equilibrium with the chloride immediately. Various other methods of treatment showed that if the electrode was first cleaned with emery cloth and then immersed, until gassing freely, in a solution of nitric acid (1 : 1) to which a little sodium nitrite had been added, it assumed equilibrium immediately on being immersed in the chloride solution, and the potential alteration on addition of the first drop of silver nitrate was very small—never more than about 8 millivolts. Electrodes treated in this way are quite trustworthy, and were used for all the electrometric titrations.

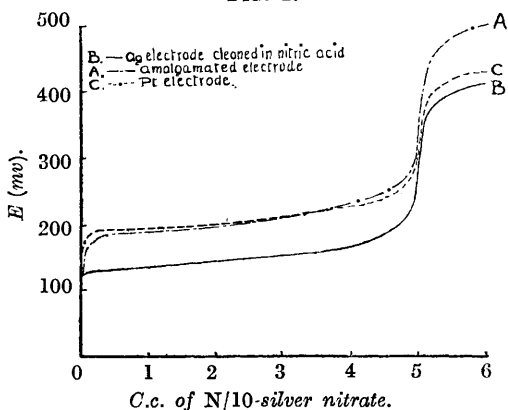
The effect of amalgamating the electrode was next tried. Amalgamation was effected by cleaning the electrode with emery cloth and then rubbing it with mercury by means of a wad of cotton wool on a glass rod, under dilute nitric acid. With such an electrode equilibrium was established in a very short time, but the first addition of silver nitrate produced a big jump in potential, equal to 70 mv. After this, the titration curve proceeded in a normal manner, giving the same end-point as the plain silver electrode. The whole curve, however, was shifted in the direction of a higher *E.M.F.* compared with the plain silver electrode curve; *i.e.*, it was more "noble." This is shown in Fig. 2. Similar results were obtained in the titration of bromides and iodides.

This suggested a new method of titrating halides with silver nitrate by means of a bimetallic electrode system, the use of a calomel cell thus being eliminated. If two electrodes, one of amalgamated silver and the other of plain silver, are immersed in a chloride solution to be titrated, the resulting titration curve should be the difference between curves A and B in Fig. 2. This difference is practically constant until, in the neighbourhood of the end-point, a deviation occurs, giving a sharp break in the curve. after which it becomes constant again. Measurements showed that this method affords a means of determining a halide as accurately as the other methods used. The breaks at the end-point are very sharp and the magnitude



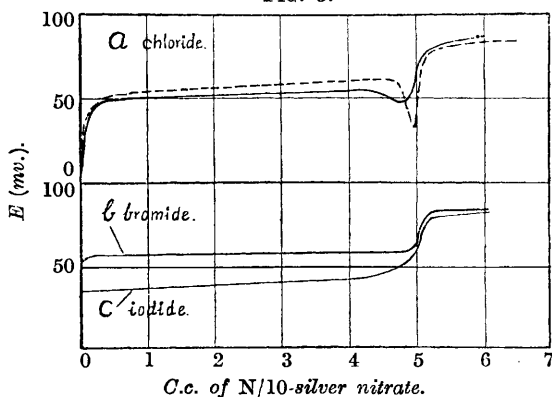
of the jumps in the case of chloride, bromide, and iodide are about 30—40 mv. Fig. 3 shows titration curves for chloride, bromide, and iodide. In the neighbourhood of the end-point, it is necessary to allow a minute or so for equilibrium to be attained after each addition of silver ions.

FIG. 2.



The dotted curve in Fig. 3 (a) is the curve calculated by subtracting the two curves A and B of Fig. 2. It agrees well with the curve obtained by direct titration with the bimetallic system. In the case of chloride only, a drop in the curve is observed in many cases,

FIG. 3.



before the final jump, although in some chloride titrations this drop is absent. The end-point of curves which exhibit this drop is at the point of maximum slope of the final jump. All curves obtained by this bimetallic method exhibit an initial jump on the first addition of silver ions, owing to the amalgamated electrode always

showing such a rise. The method has not yet been applied to mixtures of halides. In the titration of iodides, the curves with plain silver and with amalgamated silver were actually coincident for some distance at the end-point, and yet the bimetallic titration showed a marked jump at the end-point. Müller (*Z. Elektrochem.*, 1924, **30**, 420) appears to think that if the curves are tangential the potential should drop to zero at the end-point; but this is not necessarily so.

In many cases of normal titration with a silver wire and calomel cell, some time, often  $\frac{1}{2}$  hour, is required for the attainment of equilibrium of *E.M.F.* in the immediate neighbourhood of an end-point, especially in titrations with very dilute silver nitrate. During this time, the potential rises, rapidly at first, then more slowly, and finally reaches a steady value. This change corresponds with what is equivalent to a slow increase in silver-ion concentration, and obviously is not due, therefore, to the silver ions taking a long time to react with the halide ions remaining. It appears to be due to the time taken for the silver electrode to assume equilibrium with the changed concentration of silver ion.

If an electrode which has been used for one titration of halide is not scraped clean and treated with nitric acid before being used again, the *E.M.F.* found for the new system before the addition of any silver ions is somewhat higher than when a freshly-cleaned electrode is used, and the initial potential jump is very small. The electrode seems to be "formed" in some way, during the first titration.

Good titration curves giving correct end-points are obtained if a bright platinum wire instead of a silver wire is used in conjunction with a calomel cell (compare Müller, *Z. Elektrochem.*, 1924, **30**, 420). The curve shows an initial jump of about 40 mv., and lies above the curve for the silver electrode, as shown in Fig. 2. Attempts to use a bimetallic electrode system of platinum and silver gave very poor results, which were useless in practice.

#### *Titration of Mixed Halides.*

The solubility products of the silver halides are of the order : silver chloride,  $10^{-10}$ ; silver bromide,  $10^{-12}$ ; silver iodide,  $10^{-16}$ . Theoretically, then, if silver nitrate is added slowly to a mixture of, say, bromide and chloride in solution, precipitation of the bromide should be complete before that of the chloride begins. In practice, this does not occur; some chloride is precipitated along with the bromide before all the bromide is thrown down, and if a mixture of bromide and chloride in water is titrated electrometrically with silver nitrate, an error in the values is found.

That the individual halides cannot be separated quantitatively from a mixture of halides by addition of silver nitrate has long been known. It has been commented on by many workers, including Foerster ("Elektrochemie Wässrige Lösungen," 3rd edn, 1922, p. 165), Mellor ("Treatise on Inorganic Chemistry," Vol. III, pp. 418—419), Sheppard and Trivelli ("Silver Bromide Grain of Photographic Emulsions," 1921, pp. 42 *et seq.*), Küster (*Z. anorg. Chem.*, 1898, **19**, 81), Küster and Thiel (*ibid.*, 1900, **23**, 25), Thiel (*ibid.*, 1900, **24**, 1), and Müller ("Elektrometrische Massanalyse," 2nd edn, 1923).

The electrometric titration curve of a mixture of two or three soluble halides with silver nitrate shows a sudden break in the neighbourhood of the end-point of each halide, the iodide break occurring before the bromide break, which comes before the final chloride break. The arguments which apply to any pair of halides are obviously applicable to titration of a mixture of all three, so only pairs of halides will be considered at first. If a mixture of chloride and bromide in water, with no other additions, is titrated with silver nitrate, the bromide end-point appears too late, whilst the final break appears in its true position. This results in a correct estimate of the total halide, but a too high value for bromide and a too low value for chloride. The same applies in the case of bromide-iodide mixtures. With chloride-iodide mixtures the error is practically non-existent. It seems to be the general opinion that the end-point error is due to the formation of solid solutions as described by Küster and Thiel (*loc. cit.*), adsorption phenomena playing a preliminary rôle.

According to Dutoit and von Weisse (*J. Chim. Phys.*, 1911, **9**, 630) iodide can be accurately titrated in presence of a large excess (600 times or more) of chloride or bromide. This is true for iodide in chloride, but certainly not for iodide in bromide.

The end-point error increases in the series: chloride-iodide < bromide-iodide < chloride-bromide, being larger the less the solubility difference between the silver salts corresponding with a pair of halides. The magnitude of the error in the case of bromide-chloride and bromide-iodide mixtures is indicated by the following figures:

C.c. of halide solutions in terms of N/10-silver nitrate.			
Theoretical.		Found.	
Chloride.	Bromide.	Chloride.	Bromide.
{ 5.05	5.05	4.5	5.6
{ 5.05	5.05	4.6	5.5
Bromide.	Iodide.	Bromide.	Iodide.
{ 5.15	5.05	5.0	5.2
{ 5.15	5.05	5.0	5.2

Two methods were tried for eliminating this error, namely : (1) working in very dilute solution, and (2) adding certain neutral substances to the titration solution.

The effect of dilution was examined on the titration of a bromide-iodide mixture. Diluting to 330 c.c. instead of the 50 c.c. normally employed in the titrations resulted in an increase in the error.

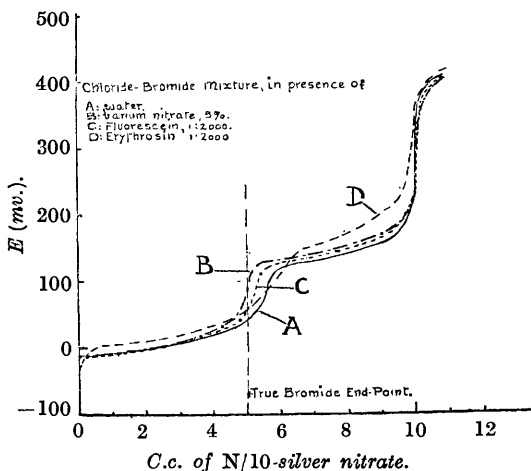
The correction of the end-point error by adding ions which are strongly adsorbed by silver halides has been studied in detail by Müller (*op. cit.*), who titrated in the presence of 5% barium nitrate solution and found that this salt prevents, or at any rate limits, the formation of solid solutions, so that the end-point error is practically eliminated. Müller writes : "The accuracy of estimation of iodide in the presence of bromide and of iodide in the presence of chloride is good in all cases in presence of 5% barium nitrate. Even the estimation of small amounts of one halide in presence of excess of the other is not affected. . . . In the estimation of bromide and chloride in the presence of one another, we must, unfortunately, reckon on an error of 1% too much bromide and correspondingly too little chloride, if equal molar concentrations of both are taken. This error increases with increasing excess of chloride, and falls off with increasing bromide excess . . . until it can be neglected when the molar concentration of bromide exceeds that of chloride by five times." Müller also mentions potassium alum in the same connexion as barium nitrate, but gives no data concerning its action. According to Foerster (*op. cit.*), in presence of barium nitrate, iodide in a ratio of iodide : bromide  $> 1 : 3600$  can be estimated accurately, but bromide in chloride only when bromide : chloride = 1 : 10.

It appears that adsorption effects of some type are responsible for the end-point error. The exact nature of this adsorption is not quite clear, although it is probable that in the case of iodide-bromide mixtures, for example, it is adsorption of silver bromide to silver iodide which is concerned. It cannot be mere adsorption of bromide ions, because a certain amount of silver ions is involved ; also it is improbable that it is adsorption of silver ions alone. It is most likely adsorption of silver bromide itself (probably colloidal), rather than the formation of a solid solution in the usually accepted sense.

Numerous measurements substantiated Müller's observations that correct end-points are obtained in presence of 5% barium nitrate solution. Lottermoser used ammonium nitrate to remove adsorbed silver from silver halides, and Fajans and his co-workers (Fajans and Hassel, *Z. Elektrochem.*, 1923, **29**, 495; Hassel, *Kolloid-Z.*, 1924, **34**, 304) studied the adsorption of dyes, and

adsorption replacement by dyes, on silver halides, with particular reference to a titration method for halogen and silver using fluorescein and its halogen-substitution products as indicators. These and other substances, including some which are known to be strongly adsorbed by silver halides, were investigated by the author. Since the end-point error is most marked in the case of bromide-chloride mixtures, in some cases only this mixture was investigated; in others, iodide-bromide mixtures were studied as well. The method of examination in most instances was to titrate with *N*/10-silver nitrate a mixture of 5.0 c.c. of a *N*/10-solution of each of the halides in the presence of 50 c.c. of the solution of the substance investigated.

FIG. 4.



*Dyestuffs.*—Erythrosin (1 in 2000), fluorescein (1 in 2000), and rose Bengal 3 (1 in 2000) gave correct end-points with the bromide-iodide mixtures. In the case of the chloride-bromide mixture, fluorescein (1 in 2000) gave a partial correction, as shown in curve C, Fig. 4. With erythrosin (1 in 2000), the final end-point for the mixture was accurate and was marked by a definite jump in potential, but the first break, representing the bromide end-point, was flattened out. In Fig. 4, curve D is a titration curve obtained in presence of erythrosin (1 in 2000). Similar results were obtained in presence of safranin (Bayer, 1 in 1000). Curve A (Fig. 4) shows the curve in presence of water alone, and curve B the correct curve, in presence of 5% barium nitrate.

Correct end-points for both chloride-bromide and bromide-iodide mixtures were obtained with 5% solutions, not only of

C C\*

barium nitrate, but also of ammonium nitrate, sodium nitrate, and sodium acetate. The results with sodium acetate show that the effect is not due to the nitrate ion, and this was confirmed when it was found that *N*-sulphuric acid also gave practically complete correction.

A solution of 3.5*N*-nitric acid, with a platinum electrode, gives correct end-points with bromide-chloride mixtures, but at the final break the curve begins to rise sharply and then drops suddenly back, after which it tends to become horizontal. The system is rather insensitive and the potential readings are jerky and can be read only to the nearest 2 or 3 millivolts.

*N*/10-Nitric acid, with a silver electrode, gives correct end-points, and is very sensitive. For accurate work, involving a long titration time, it is conceivable that an error could be introduced owing to action of the acid on the silver electrode, but with ordinary titrations of a mixture of equivalent proportions, no error was observed. A platinum electrode is unsatisfactory with *N*/10-nitric acid.

It follows from the foregoing that although the presence of certain dyes is beneficial in the case of bromide-iodide mixtures, they are not of general value. On the other hand, barium, sodium, and ammonium nitrate, and sodium acetate in 5% solution give correct end-points with bromide-chloride and bromide-iodide mixtures for a wide variation in the proportions of the constituents of the mixtures. The presence of these salts curtails the titration time by increasing the sensitiveness of titration and lowering the time required for equilibrium potential in the region of the end-points; even for the titration of a single halide in solution their presence is beneficial. In absence of added salts, the silver halides formed in the titration remain in colloidal suspension until the final end-point is reached; if a salt is present, however, the silver halides begin to precipitate shortly after the first addition of silver nitrate.

The original object of this investigation was to study the applicability of electrometric methods to the examination of materials used in the manufacture of photographic emulsions, and to the analysis of emulsions themselves. In all the titrations made, this object was borne in mind. Consequently, in the examination of bromide-iodide mixtures, for example, low percentages of iodide in bromide were considered, rather than low percentages of bromide. A series of mixtures was studied in various circumstances to ascertain if it was easy to estimate a low percentage of one halide in the other. A limit of 0.2% of iodide in bromide and of chloride in bromide was set. The following table shows some results of measurements. The percentage composition refers to equivalents of one halide in another. The substances mentioned in the column

headed "Notes" were added to the electrolyte, 50 c.c. of a 5% solution being used in each case.

Mixture taken.	Vol. in c.c. of <i>N</i> /10-conc.	Found.	Notes.
100% Bromide.	5, 10	100% Bromide.	Same results in water, barium nitrate, sodium acetate, etc. Barium nitrate, etc., <i>must</i> be present.
100% Chloride.	5, 10	100% Chloride.	
100% Iodide.	5, 10	100% Iodide.	
50% Chloride in bromide.	10	50% Chloride.	
1.01% Chloride in bromide.	10	0.99% "	Barium nitrate.
0.51% " "	10	?	Sodium acetate; breaks in curve not separ- ated.
0.50% " "	20	0.50% "	Barium nitrate.
0.2% " "	50	<0.25% " about	Sodium acetate.
0.2% " "	50	0.1% "	" "
0.2% " "	100	0.19% "	" "
0.2% " "	100	0.22% "	Barium nitrate.
50% Iodide in bromide.	10	50% Iodide.	Barium nitrate, etc.
1.6% " "	10	1.5% "	Barium nitrate.
0.19% " "	10	0.2% "	" "
50% Chloride in iodide.	10	50% Chloride.	In water alone; more sensitive in presence of barium nitrate, etc.
0.2% " "	50	0.2% "	75 C.c. of 5% am- monium nitrate.
0.2% " "	50	0.18% "	75 C.c. of 5% am- monium nitrate.

The table shows that it is possible to estimate 0.2% chloride in bromide or iodide, and 0.2% iodide in bromide, with a fair degree of accuracy. The bulk of the halide was precipitated with *N*/10-silver nitrate, but for the estimation of halide present in the proportion of 1% or less, *N*/100- or *N*/1000-silver nitrate was used, an *N*/10-solution being employed only for precipitating the bulk of the halide in excess. The accuracy of estimation of a small percentage of one halide obviously depends on its absolute amount. If the absolute amount is too small, it becomes impossible to estimate the chloride present in low ratio at all, because no distinction is observed between the two breaks in the curve. Using a mixture of *N*/10-strength, it is possible to estimate 0.2% chloride in iodide with 50 c.c., but in the case of 0.2% chloride in bromide, if 50 c.c. are used the breaks in the curve are not separated, and at least 100 c.c. must be taken.

The estimation of low percentages of chloride in iodide or bromide thus involves taking a big bulk of material; this makes the titration very long, and introduces a possible source of error in that some of the chloride solution may be occluded in the bulky silver bromide or silver iodide precipitate. Means were therefore sought by which

the bromide or iodide could be destroyed, at the same time leaving the chloride free in the solution, where it could be titrated.

Numerous methods have been devised for estimating mixtures of halides in which one halogen is removed by oxidation of its halide salt, leaving the other halide intact. Considering a chloride-bromide mixture, however, it is very probable that in the region of the point where practically all the bromide had been destroyed, some of the chloride would be attacked as well. A satisfactory method of operation would be to react with insufficient oxidiser to destroy all the bromide present, leaving, say, equal proportions of bromide and chloride, and then to titrate this mixture electrometrically in the usual way. In this manner, a big bulk of mixture, in which the absolute amount of chloride is high enough for the accuracy required, can be used without the disadvantages already mentioned. There seems theoretically to be no limit to the minuteness of the trace of chloride which could be estimated in this way.

Attempts to destroy all the bromide by means of ammonium persulphate (Engel. Compare Crookes's "Select Methods in Chemical Analysis," 1905, p. 558) or potassium permanganate (Winkler, *Z. angew. Chem.*, 1915, **28**, 477, 494) were not successful. In the former case all the bromide could not be destroyed, even when many times the theoretical quantity of persulphate was used, whilst in the latter case some chlorine was always lost in getting rid of the last traces of bromide. For example, a mixture of 2.3800 g. of pure potassium bromide with 0.0050 g. of potassium chloride in 350 c.c. of water was analysed by Winkler's permanganate method, and 0.0038 g. of chloride was found instead of 0.0050 g.

Using just insufficient permanganate to react with all the bromide proved to be a very suitable and accurate means of determining low percentages of chloride in iodide and bromide. The procedure is best illustrated by an actual example, as follows: A mixture of 2.3800 g. of potassium bromide and 0.0050 g. of potassium chloride was dissolved in 350 c.c. of water, 25 c.c. of concentrated sulphuric acid were added, and the whole was boiled. A solution of  $N/2$ -chloride-free potassium permanganate was prepared. A blank test having shown that 43.5 c.c. of this solution were necessary to give a permanent pink colour with the halide mixture used, 43.0 c.c. of permanganate were added slowly to the boiling acidified halide solution, and boiling was continued until all the bromine was removed and the solution became colourless. Ammonium nitrate (10 g.) was dissolved in the solution, which was then cooled and titrated electrometrically with  $N/100$ -silver nitrate. The result was: chloride taken, 0.0050; found, 0.0051 g.



The presence of manganous salts in the titration beaker does not affect the titration adversely in any way. Owing to the presence of sulphuric acid in the solution, it is preferable to add ammonium nitrate or sodium acetate, rather than barium nitrate, for the titration. Although a titration carried out with barium sulphate present gave accurate results, its presence is best avoided if the possibility of occlusion is to be eliminated.

*Estimation of Low Percentages of Bromide in Chloride.*

Although percentages of chloride in bromide from 50% down to 0.2% have been shown capable of accurate estimation, very low percentages of bromide in chloride cannot be accurately determined by direct electrometric titration. It has been found quite impossible, by direct methods of electrometric titration, to determine bromide present to the extent of less than 5% in chloride.

The following observations were made with 5% bromide in chloride of *N*/10-strength: (a) with 20 c.c. of mixture + 150—200 c.c. of 5% ammonium nitrate titrated with *N*/100-silver nitrate, a curve was obtained, with no sign of a sharp break, but merely a slight increase of slope over a long range of c.c. silver nitrate added.

(b) (a) was repeated in presence of saturated ammonium nitrate solution with the same results.

The absence of a sharp break is peculiar. When a mixture of, say, equal proportions of chloride and bromide is titrated, the composition varies until it passes through a stage at which there is 5% bromide in chloride, and yet a sharp bromide end-point is obtained. The only difference between this and the cases (a) and (b) above is that there is a bulk of silver bromide present, owing to precipitation of the first 45% of bromide.

(c) In order to simulate these conditions, 20 c.c. of *N*/10-ammonium bromide were titrated to the end-point with *N*/10-silver nitrate. 20 C.c. of *N*/10-5% bromide in chloride were then added, and the titration was continued with *N*/100-silver nitrate. The same results were found as in (a) and (b). By plotting the curves of (a), (b), and (c) on a more closed scale, a fairly sharp increase of slope was observed in the neighbourhood of the theoretical end-point, but it was impossible to locate the end-point with any degree of certainty.

Titration with *N*/100-silver nitrate is thus useless for determining 5% of bromide in chloride. The only way of obtaining satisfaction seemed to be to work with a higher concentration of silver nitrate, and a bigger bulk of halides.

(d) 10 C.c. of 5% bromide in chloride + 50 c.c. of 5% barium nitrate, titrated with *N*/10-silver nitrate, gave a sharp break at

0.5 c.c. of silver nitrate, the theoretical value. The degree of accuracy to be expected with a titre of 0.5 c.c. is, however, low.

(e) (d) was therefore repeated with 100 c.c. of 5% bromide in chloride. Solid ammonium nitrate was dissolved in this, and it was titrated with  $N/10$ -silver nitrate. A definite break was obtained in the titration curve, and its inflexion point being taken as the bromide end-point, the theoretical bromide value was found. A quotation from Müller has already been cited, in which he states that bromide cannot be accurately determined in presence of chloride, unless the molar concentration of bromide exceeds that of chloride by five times.

As shown above, however, it is possible to estimate 5% bromide in chloride of  $N/10$ -strength by titration of 100 c.c. with  $N/10$ -silver nitrate. Percentages less than 5 cannot be so estimated with any degree of accuracy. The difficulty could probably be overcome by adding a known amount of bromide to adjust the ratio of  $\text{Br}^- : \text{Cl}^-$  to 1 : 1, titrating this mixture, and obtaining the original bromide by difference. The objection to this seems to be that any error in the titration of the total halide would be thrown on to the small percentage of bromide originally present.

Müller ("Elektrometrische Massanalyse," 2nd edn, 1923, p. 95), titrating 5% bromide in chloride directly, got accurate results\* in presence of barium nitrate, but a + 16% error in the bromide in absence of barium nitrate. With a 2.5% bromide in chloride he got an error of + 16% in presence of barium nitrate, and + 36% in absence of added salts. These results have been substantially confirmed in the experiments described here.

To estimate low proportions of bromide in chloride it thus appeared necessary to isolate the bromide as bromine either free from chlorine, or else with such an amount of chlorine as to give a preponderance of bromine, convert the bromine (and chlorine) into bromide (and chloride), and then titrate the bromide electrometrically. The presence of a small amount of chloride from chlorine carried over with the bromine will not be harmful, since, as has been shown, low ratios of chloride in bromide can be readily estimated.

Removal of bromine with bromate in acid solution was first tried. The method was satisfactory for 28.6% bromide in chloride, but for 1% bromide, it gave very variable results, and was therefore abandoned.

The use of permanganate proved to be satisfactory. The apparatus consists of a conical flask fitted with a stopper (preferably

\* This appears from Müller's table (p. 95) to be just a chance accuracy, and is contradictory to a statement by Müller quoted earlier in this paper.

of glass, ground in) carrying a graduated tap funnel for the permanganate, and a tube with a trap, leading to a vertical condenser dipping into ammonia in a receiving flask. The bromide-chloride mixture is put in the conical flask together with plenty of sulphuric acid and boiled. Permanganate is run in drop by drop until the pink colour persists for a short time, and then a further addition of about the same volume of permanganate is made, and the solution is boiled for some time, until it loses its colour. The ammonia in the receiver is acidified, ammonium nitrate added and the solution titrated as usual. The following figures show that this method is capable of a fair degree of accuracy :

Mixture examined.	Bromide in chloride.	
	Theoretical %.	% Found.
200 C.c. of 1% bromide in chloride ( <i>N</i> /10).	1	(1) 0.95 (2) 0.9
40 C.c. of 0.5% bromide in chloride ( <i>N</i> /10).	0.5	0.49

A further attempt to estimate bromide in chloride was made using the method of Willard and Fenwick (*J. Amer. Chem. Soc.*, 1923, **45**, 623), in which the halides are mixed with potassium cyanide solution and sulphuric acid and titrated electrometrically to the CNBr end-point with permanganate solution. The method was tried with a platinum electrode and calomel cell, but the potential readings were very inconsistent and jerky, and the rate of attainment of equilibrium of potential was very variable. The method of Willard and Fenwick depends on the same reaction as that employed by Müller and Schuch (*Z. Elektrochem.*, 1925, **31**, 332) for estimating halogens in solution by electrometric titration with cyanide. Various modifications of this method were tried without success.

The ingenious method of "differential titration" due to Cox, already mentioned, was investigated for the titration of bromide with silver nitrate, and good results were obtained. An example of the method used is as follows : 10 c.c. of *N*/10-bromide + 200 c.c. of water were put into each of two beakers. The solutions were united by a bridge of saturated ammonium nitrate solution, and silver electrodes were immersed one in each solution and connected to the potentiometer. The two solutions were titrated simultaneously with *N*/10-silver nitrate from two burettes, one being kept 0.2 c.c. ahead of the other, the *E.M.F.* being measured after each addition of silver nitrate as usual. A very sharp maximum was obtained, and equilibrium was practically instantaneous. Bromide found = 20.1 c.c.; theoretical = 20.14 c.c. of *N*/10-Ag. The method is thus satisfactory for plain bromide solution. Its advantages are that it eliminates the use of the calomel cell, and

equilibrium is instantaneous at the end-point. Its disadvantage is that manipulation of two burettes is necessary. On the whole, however, it appears to possess no ultimate advantage over the ordinary method.

The differential method was tried for the estimation of 1% bromide in chloride, but without success. At the bromide end-point the curve certainly tended to a maximum, but this could not be definitely located.

#### *Estimation of a Mixture of Three Halides.*

Since a pair of soluble halides can be estimated accurately under certain conditions, it is to be expected that a mixture of three halides could just as accurately be determined under similar conditions.

A mixture containing 3% iodide and 1% chloride in  $N/10$ -bromide was examined. This ratio represents possible proportions of halide in a photographic preparation. 20 C.c. of the mixture + 200 c.c. of 5% barium nitrate solution were taken; the bulk was titrated with  $N/10$ -silver nitrate and the end-points were determined with  $N/100$ -silver nitrate. Taken: bromide, 19.48; chloride, 0.23; iodide, 0.59. Found: bromide, 19.48; chloride, 0.22; iodide, 0.59 (the figures denote equivalents of  $N/10$ -silver nitrate).

#### *Analysis of Silver Halides.*

In the analysis of silver halides by electrometric methods, two methods of procedure are possible. The first is to dissolve the silver halides in a suitable solvent and titrate directly the solution obtained. The second method is to set free the halogen from the silver halides in the form of soluble halides, which can be readily titrated by the normal methods.

The only method of the first type known to the author is that due to Müller (*Phot. Ind.*, 1924, 305, 332). The silver halides are dissolved in a slight excess of potassium cyanide solution, and the resulting solution is titrated electrometrically with silver nitrate. The theory of the titration and the method of deducing the results are lucidly described in Müller's original paper. Müller claims satisfactory results in the titration of a single silver halide, and with mixtures of silver iodide with silver bromide or silver chloride. Numerous measurements made to check the accuracy of the method have fully substantiated Müller's claims. The method suffers, however, from a serious limitation in that it does not distinguish between silver bromide and silver chloride. In the analysis of many photographic materials this should be of no account, since the majority of fast plates should consist entirely of silver bromide

and silver iodide mixtures. In the case of some plates, however, chloride is added in addition to the other two halides, and in most cases chloride is present unintentionally because the soluble iodide and bromide used in making the emulsions are rarely, if ever, free from chloride. For the analysis of chloro-bromide emulsions, Müller's method would obviously be unsuitable.

Owing to the limitations of Müller's method, the second type of method, in which the silver halides are converted into soluble halides, was investigated. Samples of pure silver halides were first prepared in the following manner. The preparations were carried out in red light, and the products were stored in dark brown glass bottles.

*Silver chloride* was prepared by adding silver nitrate drop by drop to a vigorously stirred solution of pure potassium chloride until the slightest excess of chloride remained. The precipitate was washed many times with water, and drained by suction. One sample of chloride was dried in a desiccator, but formed such hard lumps that it could not readily be dissolved in cyanide solution. The moist preparation was therefore used.

*Silver bromide* was prepared from a sample of commercial potassium bromide containing about 1% of chloride. It was dissolved in 5% ammonium nitrate solution, and silver nitrate, also in 5% ammonium nitrate solution, was run in drop by drop, the whole being vigorously stirred. Silver nitrate equivalent to 14/17 of the bromide was added during 3 hours. The precipitate was washed five times by decantation, collected, and dried in a desiccator.

*Silver iodide.* Part of the damp sample made for the preparation of pure soluble iodide, as described earlier, was dried in an electric oven at 105°.

#### *Conversion of the Silver Halides into Soluble Halides.*

Two methods of reduction of the silver halides to give the halogen in the form of soluble halides were investigated: (a) Direct reduction of the solid silver halide. (b) Reduction of the silver halide in solution.

*Method (a).*—The simplest method of getting the halide in the soluble form is direct reduction of the solid silver salt by a substance such as hydroxylamine. For electrometric titration it is necessary that the excess of the reducing agent be rendered harmless in some simple way which does not involve any loss of halogen.

Destruction of any excess of hydroxylamine could be satisfactorily carried out by gentle ignition with excess of alkali at about 200°. Oxidising agents, which would probably cause loss of halogen, should not be used.

Formic acid was unsuitable as a reducing agent, even on prolonged boiling with the silver salts. Reduction was far from complete, and chocolate-brown products resembling the synthetic photo-halides were formed. Hydroxylamine sulphate in alkaline solution was very efficient, but the reduction of solid silver halides by its means, even on very prolonged stirring, was incomplete in the majority of cases. The spongy silver mass obtained invariably contained traces of unreduced silver halide, which could be detected by dissolving the silver in nitric acid. Attempts were made to peptise the silver halides before reduction and thus render the reduction quantitative. Octyl alcohol was useless for this purpose. Addition of a known excess of potassium iodide gave a finely-divided suspension in the case of silver iodide, but the excess of halogen ions slowed down the rate of reduction so much as to render its use impracticable.

Boiling a suspension of silver iodide in water with zinc and dilute acetic acid gave incomplete reduction.

*Method (b).*—Reduction of the solid halide having proved useless for obtaining quantitative conversion to soluble halide, the reduction of the solution of the silver halides in potassium cyanide solution was investigated. A solution of silver iodide in cyanide was treated with (a) alkaline hydroxylamine, (b) alkaline hydrazine hydrate, (c) sodium hydrosulphite [hyposulphite], and (d) diaminophenol (amidol). With (a) there was no reduction in 18 hours, and with (b) in the same time, only a trace of action. Hydrosulphite reduced the solution directly to silver; and amidol caused reduction on long standing, but there was simultaneous formation of undesirable oxidation products.

When hydrosulphite is added to a solution of silver iodide in cyanide, precipitation of the silver iodide first occurs, and this is followed rapidly by its reduction. If the solutions are too concentrated, coagulation of the silver iodide occurs before it is reduced, and results in a part of the silver halide inside the curds remaining unreduced. Complete reduction of the silver halide can be effected by working in dilute solution, and adding the hydrosulphite solution a little at a time. On each addition a yellow colloidal solution of silver iodide forms. The next addition of hydrosulphite should not be made until reduction of the colloidal suspension due to the previous addition begins.

Attempts were made to prevent coagulation of the silver iodide by adding colloids before reduction. Gelatin and gum arabic effectively prevented coagulation, but their use resulted in the formation of a protected colloidal silver sol on reduction, and this could not be removed by filtration, even after prolonged boiling

with electrolytes. More satisfactory results were obtained with dextrin; the silver formed on reduction with hydrosulphite readily coagulated on boiling, and could be filtered off.

The excess hydrosulphite can be destroyed by boiling with acid, which also removes all the cyanide ions, and the solution of soluble halides is then ready for titration, after addition of barium nitrate or other salt.

Almost all commercial samples of sodium hydrosulphite contain appreciable quantities of chloride. This makes the hydrosulphite method dependent on the ability to obtain the chloride-free product, the application of a correction for chloride being undesirable. Attempts made to prepare pure hydrosulphite as required, *e.g.*, by passing sulphur dioxide gas into water containing metallic zinc, or into a solution of sodium sulphite containing zinc were not satisfactory. Combination of the two operations of preparing hydrosulphite and reducing the silver complex by passing sulphur dioxide into a cyanide solution of silver iodide containing sodium sulphite and metallic zinc did not give very satisfactory results.

*Reduction with Zinc.*—Although hydrosulphite is very satisfactory for reducing the cyanide solution, the difficulty of getting samples free from chloride led to trials with other reducing agents, of which zinc dust or granulated zinc, with acetic acid, proved very satisfactory.

Boiling the solution with granulated zinc and acetic acid gives complete reduction. On adding the acetic acid there is a tendency to form colloidal silver halide, but although in certain cases coagulation sets in, it is not of such a nature as to prevent complete reduction to silver. Addition of sodium acetate to the acetic acid, lowering the acidity to  $p_{\text{H}}$  4.8, did not prevent some silver salt being thrown out of solution.

Results as satisfactory as those obtained with granulated zinc and acetic acid are obtained by boiling with granulated zinc or zinc dust without acid, and no precipitation of silver halide occurs in these cases. It is necessary, however, to add acetic acid after the reduction is over in order to remove the excess of cyanide. The disadvantage in the case of zinc dust is that many samples contain chloride, whereas granulated zinc can be readily obtained very pure.

The conditions for titration of the reduced solution are as follows :

(1) No free cyanide must be present. This is ensured by boiling with acetic acid.

(2) Presence of free acetic acid has no adverse effect on the titration of mixed halides. In fact, sodium acetate has been shown to be advantageous.

(3) Undissolved zinc must be filtered off, otherwise further reduction will occur during the titration with silver nitrate.

(4) Zinc ions present in the titration must have no adverse effect. That they do not affect the titration was shown by control titrations to which zinc sulphate had been added.

(5) Boiling a solution of soluble halide with zinc and acetic acid must not result in loss of halogen. Blank experiments showed that no such loss occurred.

The method was then tested quantitatively, with known amounts of standard solutions of silver halides in potassium cyanide. Müller's titration method (*vide supra*) was employed for standardising these solutions. Use of this method for estimating known weights of silver halide in cyanide solution gave very accurate results, and justified its use for the standardisation of solutions. 20 C.c. of the standard solutions of silver iodide, bromide, and chloride were equivalent to 17·20, 27·10, and 7·65 c.c., respectively, of *N*/10-silver nitrate.

Both granulated zinc and zinc dust reduction gave accurate results with all three halides. The method finally used in all cases is illustrated by the following example :

Stock silver iodide-potassium cyanide solution (20 c.c.) was diluted to about 100 c.c. with water and heated, 1—2 g. of granulated zinc in small pieces were added, the solution was boiled vigorously for 10—15 minutes, 50 c.c. of acetic acid (100 c.c. of glacial acid diluted to 1 litre with water) were added, and boiling was continued vigorously until all smell of cyanide had disappeared. The solution was then cooled and decanted through a filter, the metallic residue being carefully washed several times. Ammonium nitrate was added to the combined filtrate and washings to make about 5% concentration, and titration was carried out electrometrically in the manner already described.

The quantities taken and found, expressed as c.c. of *N*/10-silver nitrate, were : silver iodide, 17·20 and 17·20; silver bromide, 27·10 and 27·10, 27·05; silver chloride, 7·65 and 7·65. The conversion of silver halide into soluble halide is thus quantitative. There should therefore be no more difficulty attending the estimation of mixed silver halides than was the case with mixtures of soluble halides already described. For this reason, exhaustive investigation of mixed silver halides was not made. For two mixtures of silver iodide and silver bromide, reduced with zinc and acetic acid, the values, in c.c. of *N*/10-silver nitrate, were : (1) Bromide : taken, 27·10; found, 27·05. Iodide : taken, 4·30; found, 4·30; (2) Bromide : taken, 27·10 found, 27·09. Iodide : taken, 0·43; found, 0·41.



*Analysis of Photographic Emulsions.*

The method described above was applied to the analysis of photographic emulsions.

Preliminary experiments were made to ascertain whether the reduction of silver halides could be satisfactorily carried out in presence of gelatin. A mixture of standard potassium cyanide-silver iodide solution, 100 c.c. of water, and 25 c.c. of 1% gelatin was heated to boiling, granulated zinc and 50 c.c. of 10% acetic acid were added, and the boiling was continued. In  $\frac{1}{2}$  hour very little reduction had occurred, and the silver halide which had been thrown out of solution was carried away from the sphere of reduction by the frothing gelatin. Several hours' boiling had not resulted in complete reduction.

In another case, the emulsion was scraped off a soaked photographic plate into water, which was heated to disperse the gelatin. Cyanide was added to dissolve the silver salts, and the whole was boiled with zinc and acetic acid. After several hours, reduction was again incomplete.

It was obvious that the presence of gelatin was to be avoided. If the emulsion is boiled with nitric acid to destroy the gelatin there is an element of risk involved, in view of the known action of nitric acid in freeing halogen from silver halides. Lehmann and Bolmer (*Phot. Ind.*, 1922, 467, 491) found that cold nitric acid above a concentration of 47%, and hot nitric acid above 5%, converts silver iodide into silver nitrate and iodine. If, however, 5% nitric acid is used for destroying the gelatin, the halide remains in suspension and cannot be filtered. The workers mentioned recommended a mixture of 4% nitric acid in 20% acetic acid for isolating the silver halide. Valenta (*Phot. Korr.*, 1914, 51, 122; "Photographische Chemie und Chemikalienkunde," I, 2nd edn, 1921, p. 151) used 20% nitric acid for destroying the gelatin. This practice is criticised by Lehmann and Bolmer, and is shown to lead to errors.

It appeared preferable to avoid the use of oxidising acids for the destruction of the gelatin, in the case of plates, at any rate. The method of fixing out the silver halides with cyanide was therefore tried, with success; this has the advantage of eliminating the need for stripping the emulsion.\*

Numerous commercial plates were investigated, to ascertain the best conditions for analysis. With plates of fast, or special rapid

\* If stripping is considered desirable, it can readily be carried out by means of alkaline sodium benzoate, prepared by dissolving benzoic acid in excess of caustic soda solution.

type, one half-plate provides a suitable quantity of material for investigation, but in the case of thinly-coated plates of the process type, two half-plates should be used.

The method of analysis finally adopted for a half-plate is as follows :

The plate is fixed out in a dish with 100 c.c. of *N*/10-potassium cyanide, and washed by soaking (5 minutes) in three changes of 100 c.c. of water. No silver salts can, in general, now be detected in the gelatin film. As a precaution, however, after washing, the plate is spotted with sodium sulphide; the absence of a brown stain indicates freedom from silver salts. The washings and fixing solution are combined, reduced with zinc and acetic acid, and treated as described for the examination of mixed silver salts. *N*/100- or *N*/10-Silver nitrate is used for titration, according to the amount of the particular halide being analysed. Owing to a slight action of the cyanide solution on the gelatin of the plate, a little gelatin sometimes goes into solution, but it only results in a somewhat slower attainment of equilibrium of potential when dilute silver nitrate is used. With *N*/10-silver nitrate, equilibrium is attained at the normal rate.

The following table shows the results obtained in the analysis of a few commercial plates. These plates were of *unknown* composition, and so no check on the results was available.

Plate.	Size.	AgI.	AgBr.	Total halide.	% AgI.
A. Special rapid.	$\frac{1}{4}$	0.41	6.74	7.15	5.73
B. " "	$\frac{1}{2}$	0.47	8.18	8.65	5.44
C. " "	$\frac{3}{8}$	0.52	13.88	14.40	3.61
D. " "	$\frac{1}{2}$	0.55	13.61	14.16	3.88
E. Process.	$\frac{1}{4}$	0.11	9.30	9.41	1.17

Plates A and B were of one brand. It does not follow from this that they are of identical composition, since variations often occur among plates of the same manufacture. Also it is improbable that the total amount of silver halide is identical on both plates. Similar remarks apply to C and D. The values in columns 3, 4, and 5 refer to c.c. of *N*/10-silver nitrate equivalent to the halides.

At the time when these measurements were made, only one emulsion of accurately known composition was available. Duplicate analyses were made of half-plates hand-coated with this emulsion, with the following results :

Plate	AgI.	AgBr.	Total halide.	% AgI.	
				Found.	Theor.
Plate 1 .....	0.81	19.83	20.64	3.92	3.95
Plate 2 .....	0.80	19.57	20.37	3.92	3.95

The method thus appears capable of giving accurate results. It possesses the great advantage of ease and comparative rapidity.

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