

## Observations on an Automatic Titrimeter

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An account is given of experimental work on the performance of a modern prototype automatic titrimeter for general analytical work. Titrations that have been made with this titrimeter include those of sulphuric, phosphoric and boric acids with standard alkali, of chlorides, bromides and iodides with standard silver nitrate solution, and of iodine, liberated from potassium iodide by potassium permanganate, with standard sodium thio-sulphate solution. Observations are made on the use of the titrimeter in the maintenance of a definite pH during the titration of fluorides with standard thorium nitrate solution.

We have recently had an opportunity of examining in the laboratory an automatic titrimeter. Our main consideration has not been that of the electronic circuits of the particular apparatus, but rather its use and adaptation to the analytical problems arising in the laboratory. The prototype instrument, shown in Fig. 1, was manufactured by Messrs. Electronic Instruments Limited, of Richmond, and consists essentially of—

- (i) A burette system, which is connected to a solenoid-operated valve that has, in effect, three operational positions in which (a) the burette delivers liquid at the maximum rate, (b) the burette delivers liquid at a slow drop-rate and (c) the flow of liquid from the burette is stopped altogether.
- (ii) The instrument, which is connected to the solenoid-valve burette tap. It is so designed that by use of the appropriate controls, titration of, for example, a known amount of acid can be carried out to a definite pH value with standard alkali delivered from the burette. The controls are such that most of the alkali required in the titration is added from the burette at the maximum rate to a pre-arranged point that is approximately the end-point. Finally, the rest of the alkali required in the titration is added at a slow drop-rate, the instrument being so designed that at the appropriate pH value chosen for the end-point, the flow of liquid from the burette automatically ceases. For example, when acid is titrated with alkali to pH 7, it is possible to use the controls in such a way that the slow drop-rate commences at about pH 4 or 5.

As titration to a definite pH value is, in effect, titration to a definite potential difference between sources of variable and constant potential, the instrument is capable of dealing with titrations involving other e.m.f. differences, for example, the titration of reducing agents with oxidising agents and the titration of halides with standard silver solution.

We have made preliminary experiments on the use of this apparatus for the titration of standard sulphuric, phosphoric and boric acids with standard sodium hydroxide solution, of chloride, bromide and iodide with standard silver solution, and of iodine, liberated by interaction of potassium permanganate and potassium iodide, with standard sodium thio-sulphate solution. Further, we have used the titrimeter for the automatic maintenance of pH at a definite value during the titration of fluoride with thorium nitrate solution.

The particular burette system that we used was such that at the fast flow-rate it delivered 25 ml of liquid in 68.5 seconds and 50 ml in 165 seconds; this compared very well with the time of flow of a 50-ml burette to British Standard 846:1952. The slow drop-rate was such that when filled with liquid to the 25-ml mark, the burette delivered 200 drops, equivalent to 6.6 ml, in 105 seconds.

The burette and titrimeter were first assembled as shown schematically in the diagram, and the instrument was used in the following manner for the acid - base titrations.

After the instrument had warmed up, the "function" switch was moved to SET ZERO and the indicator needle was adjusted to zero by the "set zero" control. The "function" switch was now moved to SET BUFFER and, with the electrodes immersed in the selected buffer and the instrument dial set to the particular buffer value, *i.e.*, 4.0 or 7.0, the indicator needle was again adjusted to zero with the "set buffer" control. This adjustment was repeated to check the settings before the solution to be titrated was placed in position and

the stirrer started. The "function" switch was now moved to the mV FALLING or mV RISING position according to the particular titration and the "fast - slow change-over" control was moved to the desired number of mV before the end-point that the slow drop-rate was to start. The automatic switch was then moved to the FAST position and the titration was completed automatically.

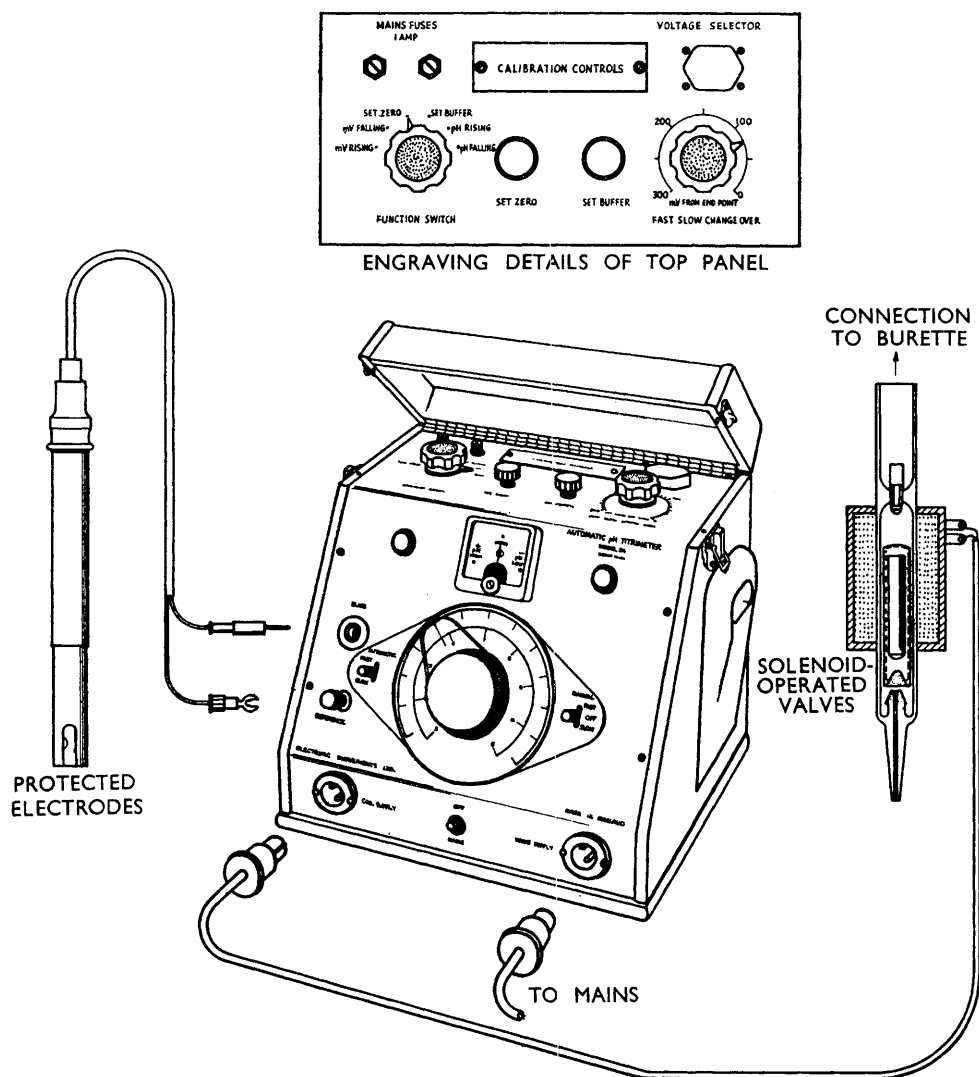


Fig. 1. The automatic titrimeter

#### TITRATION OF STANDARD SULPHURIC ACID WITH STANDARD SODIUM HYDROXIDE SOLUTION

Standard acid and alkali solutions were prepared so as to be 0.1 *N* by the ordinary methods of standardisation to indicators given in the I.C.I. scheme of standardisation.<sup>1</sup>

Titration of 25-ml aliquots of 0.1 *N* sulphuric acid solution with 0.1 *N* sodium hydroxide solution were made in triplicate, the automatic titrimeter being used at different settings of the "fast - slow change-over" control. All titrations were made to a pH setting of 7.0, with an initial volume of 100 ml in the titration vessel. The results are shown in Table I.

Titration of 40-ml aliquots of 0.1 *N* sulphuric acid were similarly carried out to pH settings of 7.0 and 4.0, and the results, shown in Table II, were determined at change-over control settings of 200 and 75 mV, respectively.

TABLE I

TITRATION OF 25-ml ALIQUOTS OF STANDARD SULPHURIC ACID WITH STANDARD SODIUM HYDROXIDE

Change-over setting, mV	Number of drops added slowly to end-point	pH immediately at end-point	Volume of 0.1 N sodium hydroxide used, ml
300	261	8.35	25.07
	269	8.92	25.11
	265	8.61	25.11
200	16	8.71	25.11
	15	8.62	25.10
	16	8.47	25.12
100	1	9.10	25.21
	2	9.15	25.20
	1	9.20	25.22

TABLE II

VARIATION OF TITRE WITH pH SETTING

pH setting	pH at end-point	Volume of 0.1 N sodium hydroxide used, ml
7.0	Immediately after end-point, pH 8.5, falling in about 1 minute to pH 7.2	{ 40.20 40.19
4.0	pH at end-point remained reasonably constant (a) 4.3 (b) 4.2	(a) 39.95 (b) 39.99

## EFFECT OF CONCENTRATION OF THE SOLUTION IN THE BURETTE—

The effect of the dilution of the alkali on the titration of the same weight of 0.1 N sulphuric acid is shown in Table III. The titrations were made at a pH setting of 7.0 with the "fast - slow change-over" control set at 200 mV and an initial volume of 100 ml in the titration vessel. The titrations were performed on 20.00 g of the 0.1 N sulphuric acid solution. The pH at the end-point was read after the solution had equilibrated for 1 minute.

TABLE III

TITRATION OF 20.00 g OF 0.1 N SULPHURIC ACID WITH SODIUM HYDROXIDE SOLUTIONS OF VARIOUS CONCENTRATIONS

Normality of sodium hydroxide	pH value of end-point	Volume of alkali used, ml
0.1	7.2	20.11
	7.3	20.10
	7.35	20.10
0.05	7.12	40.21
	7.20	40.20
	7.12	40.21
0.025	7.10	80.44
	7.12	80.46
	7.20	80.40

We have the following observations to make on the results in Tables I, II and III.

The instrument gives excellent precision in duplicate titrations under fixed conditions.

The use of more dilute solutions in the burette does not appear to improve the extent of the overshoot in terms of pH or equivalent amount of sodium hydroxide, when titrating to a pH setting of 7.0.

The cut-out at the pH setting of 7.0 corresponds to the colour-change end-point of phenol red (pH 6.8 to 8.4).

The cut-out at the pH setting of 4.0 corresponds to the colour-change end-point of methyl orange (pH 3.1 to 4.4), which was used as indicator when the standard acid and alkali solutions were standardised.

In the above titrations, owing to the size and rate of flow of the drops, the automatic titrimer overshoots the indicator end-point by about 2 drops.

## TITRATION OF STANDARD PHOSPHORIC ACID WITH STANDARD SODIUM HYDROXIDE

A solution of phosphoric acid was prepared so as to contain 9.80 g of phosphoric acid per litre as determined by standardisation by titration to sodium dihydrogen phosphate with 0.1 *N* sodium hydroxide solution, methyl orange (pH 3.1 to 4.4) being used as indicator. Titrations of 20-ml aliquots of the phosphoric acid with 0.1 *N* sodium hydroxide solution were made in triplicate, the automatic titrimeter being used at different settings of the "fast - slow change-over" control. The titrations were made to a pH setting of 4.5, with an initial volume of 100 ml in the titration vessel. The results are shown in Table IV.

TABLE IV

## TITRATION OF 20-ml ALIQUOTS OF STANDARD PHOSPHORIC ACID WITH STANDARD SODIUM HYDROXIDE

Change-over setting, mV	Number of drops added slowly to end-point	pH at end-point	Volume of 0.1 <i>N</i> sodium hydroxide added, ml
100	{ 159	4.72	20.30
	{ 162	4.82	20.32
	{ —	4.77	20.30
50	{ 25	4.88	20.30
	{ —	4.89	20.30
	{ 30	4.85	20.25
25	{ 4	5.00	20.32
	{ 4	4.89	20.30
	{ 6	4.75	20.34

The agreement between titrations is again good and the pH of the end-point is quite stable.

## TITRATION OF BORIC ACID WITH STANDARD SODIUM HYDROXIDE

A solution of borax,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , containing 3.8143 g per litre, was prepared. Then 10 and 20-ml aliquots of this solution were treated with 20 ml of 0.1 *N* sulphuric acid and this acid solution was titrated to a pH setting of 7.1, the automatic instrument being used. Next, 5.0 g of mannitol were added and the titration of the mannitoboric acid was made to a pH setting of 8.3. The difference in the two titres corresponds to the boric acid in solution. The results are shown in Table V.

TABLE V

## TITRATION OF BORIC ACID WITH STANDARD SODIUM HYDROXIDE

Volume of borax solution, ml	pH setting	pH at end-point	Volume of 0.1 <i>N</i> sodium hydroxide, ml	Difference	Theoretical difference
10	{ 7.1	7.8	18.3	4.0	4.0
	{ 8.3	9.5	22.3		
10	{ 7.1	8.1	18.6	3.8	4.0
	{ 8.3	9.6	22.4		
20	{ 7.1	7.5	16.4	8.0	8.0
	{ 8.3	9.3	24.4		

Although the difference between the two titrations to pH 7.1 and 8.3 is near the theoretical value, this is probably due to the fact that both titrations are overshoot by the same volume. The apparatus could no doubt be used for such applications by suitable adjustments of the pH setting and by use of an improved tap, so that there is less chance of overshooting the end-point at each set pH value.

## TITRATION OF FLUORIDES WITH STANDARD THORIUM NITRATE SOLUTION

As we have indicated previously,<sup>2</sup> we are interested in the determination of fluorine in organic compounds. Our method involves fusion of the compound with sodium peroxide followed by distillation of the fusion product with perchloric acid and subsequent titration of the fluoride in the distillate with standard thorium solution, after suitable adjustment of the pH of the test solution.

During the thorium titration, which is carried out at a pH value of 3, the solution tends to become acid as the thorium solution is added and it is necessary to add sodium hydroxide to maintain the pH at 3 whilst the thorium solution is still being added. In the past we have had to keep the pH constant manually, but we find that with the automatic titrimer the operation can be performed automatically. We have tried the test under ordinary experimental conditions and, with the instrument set at a pH of 3, we found that when the titration solution attained a pH of 2.9, automatic slow addition of sodium hydroxide solution occurred until the pH was re-adjusted to 3.0. Hence, by means of the automatic instrument it was possible to maintain the pH of the solution being titrated automatically so that it never dropped below 2.9. This seemed to us to be extremely useful as, with this automatic arrangement, we were able to concentrate on the real purpose of the titration, *i.e.*, the determination of the colorimetric end-point when all the fluoride had reacted with the thorium nitrate solution. This mode of operation will result in a considerable saving of time. The details of the titration and the instrument adjustments are as follows.

The instrument was first adjusted to zero and standardised to a known pH of 4.0, as described above. The solution to be titrated, *i.e.*, the distillate containing the fluoride, was placed in position in the apparatus and the burette was filled with 0.1 *N* sodium hydroxide solution. The stirrer was started and, with the instrument used simply as a pH meter, the pH of the solution was adjusted to 6.0 by the addition of *N* sodium hydroxide from a second burette. The pH was now adjusted to 3.3 by means of 0.1 *N* hydrochloric acid added from a third burette, and then 1 ml of alizarin red S indicator was added. The dial of the instrument was set at pH 3.0 and the "function" switch was turned to pH RISING. With the "fast - slow change-over" control set at zero, the automatic switch was moved to the SLOW position.

The titration of the fluoride with 0.05 *N* thorium nitrate solution from a fourth burette was now started and continued until the pH of the solution fell below 3, which automatically started the dropwise flow of the 0.1 *N* sodium hydroxide from the automatic burette. The addition of thorium solution was now stopped and not recommenced until the automatic instrument had re-adjusted the pH to 3.0, *i.e.*, after the addition of 8 to 10 drops of the 0.1 *N* sodium hydroxide solution. This procedure was continued until the end-point was shown by the colour change of the indicator.

#### TITRATION OF CHLORIDES WITH STANDARD SILVER NITRATE SOLUTION

For several years the rapid determination of chlorine in organic compounds has been extremely important in this laboratory. It is of particular value in the examination of polyvinyl chloride and related copolymers. The method that has been used successfully over the past eight years is that of Haslam and Soppet.<sup>3</sup> By this method the sample is fused with sodium peroxide and a catalyst in a stainless-steel bomb and the fusion product is dissolved in water. Excess of peroxide is removed and the solution is finally adjusted to a definite acidity with nitric acid before titration. In this titration a silver wire, in contact with a definite concentration of silver ions, is used as a source of constant potential and another silver wire, in contact with the solution being titrated, as the source of variable potential. With a known amount of water containing a definite amount of nitric acid, the potential difference between the two electrodes is balanced to give a zero reading on the galvanometer. After this adjustment, the dilute nitric acid is replaced by the solution of the fusion products. This chloride solution is now titrated with standard silver nitrate solution to the same zero reading on the galvanometer. Precautions are taken to wash the electrodes with water just before the final end-point is reached. Although this method has always been satisfactory, particular care has to be exercised so that the end-point is not overshoot when the amount of chlorine in a sample is unknown. This is liable to occur when dealing with all kinds of polymers and compounds containing chlorine.

It is true that such difficulties may be avoided after overshooting the end-point by the addition of a known amount of standard sodium chloride solution before completing the titration. Nevertheless, it has always been considered desirable to keep the method as simple as possible and to reduce the number of standard solutions to the minimum. It seemed to us that it would be possible to use the automatic titrimer in such a way as to avoid all difficulties of this kind even on absolutely unknown samples.

Accordingly, preliminary experiments were undertaken, as a result of which the following procedure was devised for use with the same electrode system.<sup>3</sup>

A weighed sample of AnalaR sodium chloride was fused with sodium peroxide and a catalyst in a stainless-steel bomb, and the fusion product was prepared in the usual manner for analysis with the addition of 1.5 ml of 2 *N* nitric acid in excess. The instrument was then adjusted to zero in the following manner. A solution consisting of 150 ml of distilled water and 1.5 ml of 2 *N* nitric acid was placed in position. The stirrer was switched off, the function switch turned to SET ZERO and the "set zero" control adjusted until the needle was at zero. The dilute nitric acid solution was now withdrawn and the sample solution, of total volume of about 150 ml, was put in position. With the dial set to -50 mV and the "fast - slow change-over" control set at 30 mV, the automatic titration was started by moving the automatic switch to FAST. When this selected potential difference, -50 mV, was reached, the flow of silver nitrate solution stopped automatically and the control switch was moved to OFF, the stirrer was stopped and the electrodes were withdrawn and washed. After they had been put into position again, the stirrer was re-started, the dial was set to zero and the automatic switch was put on SLOW. The titration was now completed automatically to the zero potential and the burette reading was taken. The final potential difference was measured to find the amount by which the end-point had been overshoot in terms of mV.

The procedure was tested on amounts of AnalaR sodium chloride unknown to the operator at the time of test. All these samples were fused with sodium peroxide. The silver nitrate solution was standardised against known weights of the AnalaR sodium chloride, which had been submitted to the complete fusion process. Appropriate corrections were made for blanks on the reagents. Further, the chlorine was determined by means of the above procedure on a standard sample of polyvinyl chloride, the chlorine content of which had already been determined by the conventional potentiometric procedure.<sup>3</sup> The results were as follows—

## STANDARDISATION—

*Determination of the blank for the catalyst, sodium peroxide and the bomb (automatic titrimeter on SLOW)—*

Set end-point, mV	Volume of 0.1 <i>N</i> silver nitrate used, ml	Overshooting of end-point, mV
0	0.21	0
0	0.18	+9
0	0.11	0

The average blank was 0.16 ml of 0.1 *N* silver nitrate.

*Titration of known weights of AnalaR sodium chloride—*

Set end-point, mV	Volume of 0.1 <i>N</i> silver nitrate used, ml	Amount of sodium chloride, g	Overshooting of end-point, mV
0	40.44	0.2362	+11
0	35.04	0.2049	+ 8

Then 1 ml of silver nitrate solution  $\equiv$  0.0058772 g of sodium chloride  
or 1 ml of silver nitrate solution  $\equiv$  0.003545 g of chloride.

## UNKNOWN SAMPLES—

Setting to stop for washing electrodes: "fast - slow," 30 mV; wash-point, -50 mV

Setting for final end-point: 0 mV

Drops to wash-point	Drops to end-point	Potential at end-point, mV	Volume of silver nitrate — blank, ml	Sodium chloride found, g	Sodium chloride taken, g
32	12	—	41.96	0.2451	0.2443
30	13	+22	11.23	0.0656	0.0652
29	12	+10	35.23	0.2059	0.2057
23	11	+16	20.54	0.1200	0.1192

*Standard sample of polyvinyl chloride—*

Instrument settings as above.

Sample, g	Volume of silver nitrate — blank, ml	Potential at end-point, mV	Chlorine content, %	Average value	Chlorine content determined by potentiometric method, %
0.2890	45.92	+ 2	56.32	56.35	56.5
0.3011	47.90	+11	56.39		



In our view this modification represents a considerable improvement and it is now possible to determine chlorine in a large number of polymeric materials and organic compounds with considerable accuracy in about 1 hour per sample. In the titration with silver nitrate there is no danger of the end-point being overshoot.

#### TITRATION OF BROMIDES AND IODIDES WITH STANDARD SILVER NITRATE SOLUTION

The performance of the automatic titrimeter was then examined for the titration of aqueous solutions of AnalaR potassium iodide and bromide with silver nitrate solution, the same electrode system and zero adjustment procedure being used as for the titration of chloride described above. From an examination of the potential curves of the titrations, however, the following equivalence points were noted and used for the end-point setting on the dial for automatic titrations.

Equivalence point for bromide,  $-50$  mV.

Equivalence point for iodide,  $-200$  mV.

The results were as follows—

##### BROMIDE TITRATION—

###### Standardisation—

Setting for wash stop: "fast - slow," 20mV  
wash-point,  $-150$  mV

Setting for end-point:  $-50$  mV

Drops to wash-point	Drops to end-point	Potential at end-point, mV	Volume of silver nitrate, ml	Potassium bromide taken, g
1	10	+80	39.25	0.4058

Then 1 ml of silver nitrate solution  $\equiv$  0.01185 g of potassium bromide.

###### Unknown samples—

Setting for wash stop: "fast - slow," 30 mV  
wash-point,  $-150$  mV

Setting for end-point:  $-50$  mV

Drops to wash-point	Drops to end-point	Potential at end-point, mV	Volume of silver nitrate, ml	Potassium bromide found, g	Potassium bromide taken, g
7	9	+70	30.36	0.3598	0.3596
22	19	+40	43.93	0.5207	0.5216

##### IODIDE TITRATION—

###### Standardisation—

Setting for wash stop: "fast - slow," 30 mV  
wash-point,  $-420$  mV

Setting for end-point:  $-200$  mV

Drops to wash-point	Drops to end-point	Potential at end-point, mV	Volume of silver nitrate, ml	Potassium iodide taken, g
50	36	$-30$	15.44	0.2560

Then 1 ml of silver nitrate solution  $\equiv$  0.01658 g of potassium iodide.

###### Unknown samples—

Settings as above.

Drops to wash-point	Drops to end-point	Potential at end-point, mV	Volume of silver nitrate, ml	Potassium iodide found, g	Potassium iodide taken, g
74	41	+75	21.45	0.3556	0.3525
104	55	$-50$	27.60	0.4576	0.4574

#### OXIDATION - REDUCTION TITRATIONS

Finally a method was developed for the use of the titrimeter in the titration of iodine, liberated by the reaction of a known amount of standard potassium permanganate solution

with acidified potassium iodide, with sodium thiosulphate solution. The procedure and results are described below.

The electrode system, namely a calomel electrode as reference electrode and platinum foil as indicator electrode, were connected to the terminals in the automatic titrimeter marked REFERENCE and GLASS ELECTRODE, respectively. With the "function" switch on SET ZERO the indicator needle was adjusted to zero with the "set zero" control. A known amount of 0.1 *N* potassium permanganate solution was placed in a 250-ml beaker and 100 ml of 0.3 *N* sulphuric acid and then 0.3 g of potassium iodide were added. The solution was diluted to about 150 ml with water and stirred in the apparatus for 1 to 2 minutes to allow the potassium iodide to react completely with the potassium permanganate. The "function" switch was now moved to MV FALLING and the following dial and "fast - slow" change-over settings were made. These settings were chosen after a study of the full potential curve of the titration—

"Fast - slow change-over," 50 mV.

End-point, +250 mV.

With the burette filled with 0.1 *N* sodium thiosulphate solution, the "automatic" switch was moved to FAST and the titration was completed automatically. The sodium thiosulphate solution was first standardised by titration in the instrument of 25.0 ml of the 0.1 *N* potassium permanganate solution and then 2 volumes of the solution, unknown to the operator at the time of test, were similarly titrated. The results were as follows—

STANDARDISATION—

Setting for "fast - slow change-over": 50 mV

Setting for end-point: +250 mV

Drops to end-point	Potential at end-point, mV	Volume of 0.1 <i>N</i> sodium thiosulphate, ml	Volume of 0.1 <i>N</i> potassium permanganate taken, ml
11	+209	25.12	25.0
10	+209	25.23	25.0

Then 1 ml of sodium thiosulphate solution  $\equiv$  0.9931 ml of potassium permanganate solution.

UNKNOWN SAMPLES—

Settings as above.

Drops to end-point	Potential at end-point, mV	Volume of 0.1 <i>N</i> sodium thiosulphate, ml	Volume of 0.1 <i>N</i> potassium permanganate found, ml	Volume of 0.1 <i>N</i> potassium permanganate taken, ml
20	+203	25.71	25.54	25.60
23	+198	35.66	35.41	35.50

The above results are quite satisfactory, and it should be realised that it is possible to use the automatic titrimeter for other oxidation - reduction titrations if the instrument is initially set to a zero reading on the dial to correspond with a previously titrated solution.

Our purpose in preparing this paper is to draw the attention of other analysts to the great possibilities of this type of automatic instrument in general industrial work. Many modifications may be made; for example, valves of different slow drop-rates can be used for different purposes. Our preliminary experiments have convinced us that instruments of this type, perhaps modified, can be used in many ways for more accurate and speedier analytical titrations.

We are indebted to Mr. Z. J. Bujwid for his assistance in these trials.

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