

## A Simple Flow Coulometric Titrimeter for the Determination of Azo-groups

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### Introduction

Azo-dyes and their precursors have always presented a considerable challenge to the analytical chemist especially, as they do so frequently, when they occur in a mixture. The choice of analytical methods becomes one of some complexity because of the fact that many of the analytically useful chemical properties of the precursors are mimicked in the dye, particularly when substituent groups are present.

Historically, this has been the case, and so many methods have been devised to determine dye concentration. For azo-dyes, the property of the precursors not imitated by the dye molecule is the azo-group which, although somewhat unreactive, does possess a chemistry and properties of its own. Use of these properties as an approach to analysis has to be judicious, however, because many of the reagents which act on the azo-group also act on other groups, e.g. titanous chloride which reacts both with azo-groups and nitro-groups. Resorting to microanalysis to determine dye purity has problems of its own: nitrogen or carbon determinations, for example, as means to determine purity would give the same result (very nearly!) for the dye as with a mixture of the two precursor amines, and azo-groups generally give a slightly low nitrogen.

Many approaches to the determination of azo-dyes/groups have been made, one such approach being titrimetry. Knecht and co-workers used successfully a number of very powerful redox reagents: chromium(II) and titanium(III) (5-7). Whilst these reagents were efficient for the purpose, they suffered a number of major drawbacks, not the least of these being their instability towards atmospheric oxygen. In these cases a special device was employed in order to prevent contact between the reagent and oxygen. This is rather a cumbersome device and has to be kept with an atmosphere of hydrogen, thus making it dangerous as well. Even with these precautions the reagents required frequent standardization.

Certain other reductions have been tried, not without some success. For example, Raney nickel has been used as a reduction catalyst by Whitmore and Revukas (11). They investigated its use with a number of dyes and were able to perform complete reductions of the azo-groups to amines. This method, as with that of Knecht (5-7), also worked with substituent nitro- and nitrosyl-groups, which led to some complications. The latter were overcome partially by Early and Ma (2) who used titanium(III) but in hydrochloric acid medium to achieve a degree of reduction selectivity.

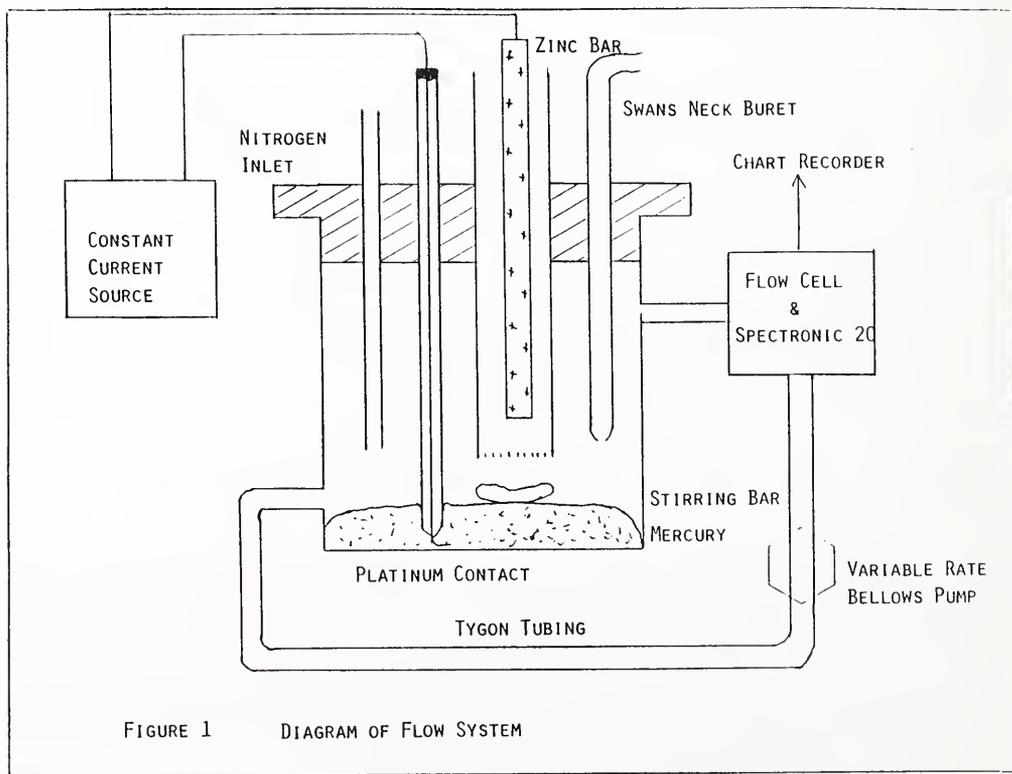
Several instrumental methods for azo-dye determination have been developed over the years. Potentiometry is one such technique: several azo-dyes have been titrated in glycerol as a solvent using Mohr's salt as the titrant (8). Flow injection analysis, a more contemporary method, which works by injection of a small quantity of azo-dye into a flowing stream of chemically generated reductant, has produced quite good results (10). Polarography was thought to be a potentially good method because of its ability to supply a continuously variable reducing voltage. It might have produced some interesting hydrazo-compounds, but generally the azo-groups underwent four-electron reductions. Cabral and Turner (1) made a fairly extensive investigation of this method but it has received little use.

Another extremely useful method for azo-dye determination is spectrophotometry, and it has been used in industry in one form or another for at least half a century (9). However, a major problem has always been one of finding a way to purify the dye (4) sufficiently for quantitative use. This difficulty has been overcome at a practical level by following the same industrial preparation process for different batches, and then accepting solutions which have the same absorbances under defined conditions (3).

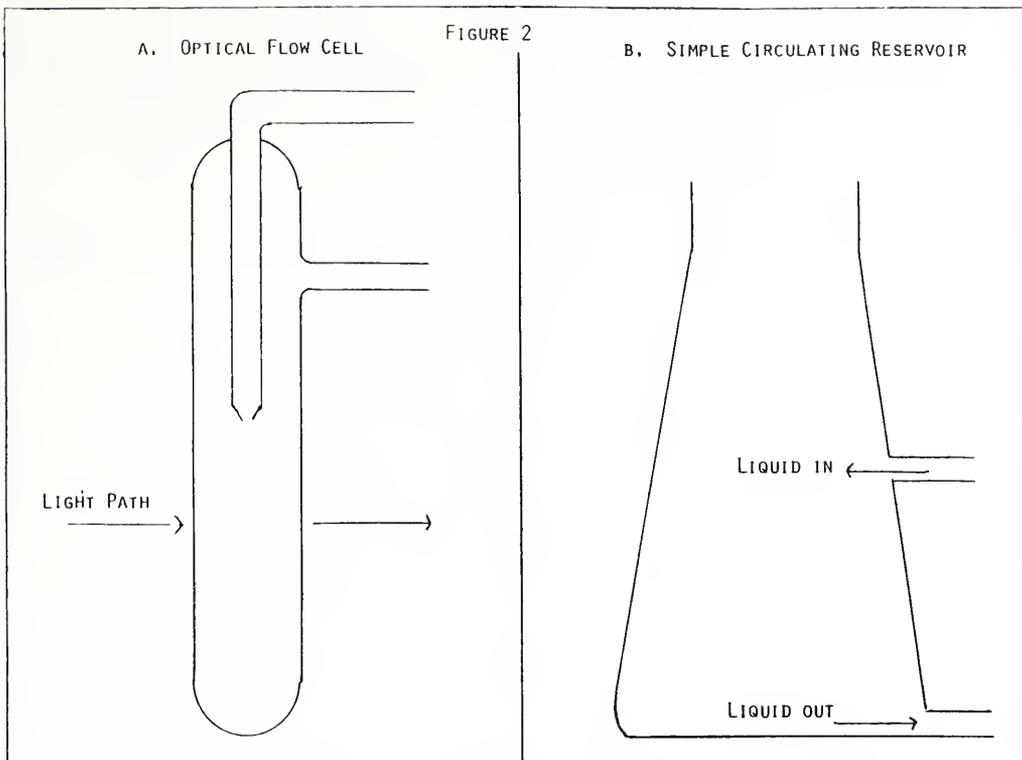
### Experimental

a) Chemicals: All chemicals used were of analytical grade, and all solutions were prepared using distilled water as the solvent. The mercury used for cathode material was distilled twice under reduced pressure and stored in a wide-necked glass bottle with a screw cap. The zinc anode was cast from 99.9% pure zinc metal and was made in the form of a bar approximately 20cm long by 1cm diameter. Acid Red 88 was synthesized specially and was at least 99.9% pure. The potassium dichromate used for titration of the titanium(III) was a primary standard material.

b) Apparatus: The apparatus design was that of a very simple flow system with provision for photometric measurement, a coulometric current supply, and sample introduction from a swan's neck buret (Figure 1). The cell was constructed from a plastic con-



tainer fitted with a stopper, the latter being bored to accept a fritted glass tube for the zinc anode, the glass insulating tube of the cathode conductor, a glass sparging tube for the introduction of nitrogen gas and a swan's neck buret. The cell was bored to accept two tubes, one at the top of the container and one at the bottom, for entry and exit, respectively, of the circulating solution. The solution in this system was pushed through the circuit by a small bellows pump (Markson Scientific) with a custom built photometric cell in series (Kontes) (Figure 2). The electrodes were connected to a constant current source (Beckman Instruments) which could be switched on as desired. A chart recorder



was attached to the Spectronic 20 (Bausch and Lomb) for the purpose of continuously recording the solution absorbance. The cathode connector was a glass tube with a short length of platinum wire sealed into one end. This end was well submerged in the mercury pool cathode and the other end was connected to the coulometer using the conventional mercury and copper wire.

c) Testing the Apparatus: The apparatus was tested in two ways: flow rate and electrolysis efficiency. In the first case, ordinary distilled water was allowed to flow through the system and a small quantity of dye solution was introduced. The time taken for the dye to mix completely, i.e. achieve a constant absorbance value, was noted for different flow rates, and ones of 25ml/min. or faster were found to promote the best mixing conditions. Subsequently, appropriate mixing/flow conditions could be selected before each experiment.

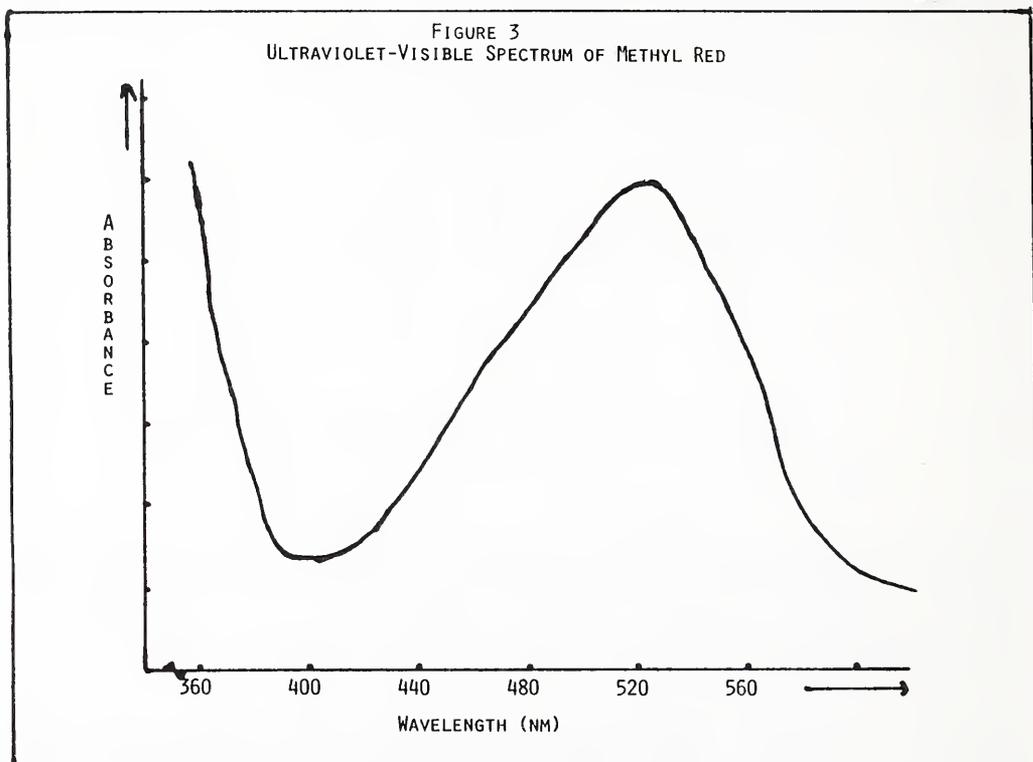
With regard to electrolysis efficiency, the cell was set up with a solution of titanium(IV) chloride in hydrochloric acid ( $\approx 4M$ ) circulating at an appropriate rate, and it was then electrolyzed for various periods of time at constant current. Throughout the electrolysis nitrogen gas was flushed through the system to provide an inert blanket of protection for the titanium(III) generated. The current was measured by putting a standard resistance across the coulometer leads and measuring the potential difference between its ends with a reliable high impedance volt meter. The most frequently used current was 99.87mA. After a period of electrolysis, a sample of the solution was removed from the cell and titrated with standard potassium dichromate solution to determine its titanium(III) concentration. The results of these tests are recorded in Table 1.

d) Performing an Experiment: In order to titrate an azo-dye, a small quantity of its solution was introduced into the cell from the swan's neck buret. Nitrogen gas was blown through the cell for a few minutes prior to commencing the experiment, and then during it as well. The spectrophotometer was set at a suitable wavelength decided upon by a previous experiment (Figure 3), and electrolysis was started. The resulting curve obtained from

TABLE I. Efficiency of Coulometric Titration\*

Time (secs)	Microeqs. Ti	Calcd. Microeqs. Ti	Efficiency (%)
210.6	217.55	217.99	99.8
268.3	275.77	277.72	99.3
179.4	184.58	185.70	99.4
239.1	245.26	247.49	99.1

\*Grand average over fifteen titrations = (99.6 + 0.3)%. This was close enough to assume 100% electrolysis efficiency throughout the experiments.



the chart recording is shown in Figure 4 along with its interpretation. Both very pure Acid Red 88 (Figure 5a) and highly impure Methyl Red (Figure 5b) were investigated in this way.

### Results and Discussion

Figure 4 shows the results of a flow experiment in which the points at which the current was turned on and off are shown. As the azo-group is reduced, the absorption due to the dye decreases until a constant value is attained. In practice the curves obtained were virtually identical to this curve. Time of electrolysis was read from both this graph and the "digital" output of the coulometer, this being the major analytical parameter; the other was the applied current, which was measured at 99.87mA for most of the experiments.

Table 2 shows the results of several experiments with extremely pure Acid Red 88 in which several different but known quantities of the dye were reduced using the electrogenerated titanium(III). The series of reactions conjectured to be involved was:

- (i)  $\text{Ti}^{4+} + e \rightleftharpoons \text{Ti}^{3+}$  (generated at the mercury cathode)
- (ii)  $\text{Zn} \rightleftharpoons \text{Zn}^{2+} + 2e$  (sacrificial anode)
- (iii)  $4\text{Ti}^{3+} + \text{-N=N-} + 4\text{H}^+ \rightleftharpoons 4\text{Ti}^{4+} + \text{-NH}_2 + \text{H}_2\text{N-}$
- or (iv)  $2\text{Ti}^{3+} + \text{-N=N-} + 2\text{H}^+ \rightleftharpoons 2\text{Ti}^{4+} + \text{-NH-NH-}$

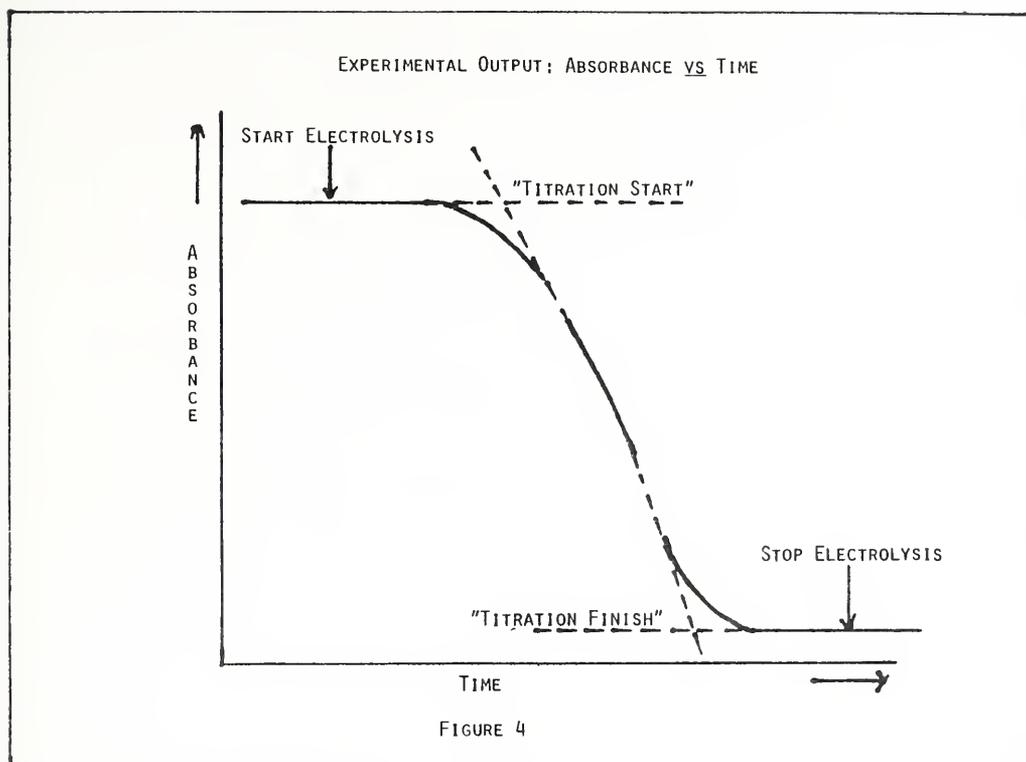


TABLE 2. Reduction of Acid Red 88\*

mls of Dye Soln.	Time (secs)	Microeqs. Dye	Number of Electrons
10.00	148.3	153.50	4.0
12.50	185.7	192.22	4.0
15.00	221.6	229.38	4.0
17.50	260.6	269.75	4.0
20.00	294.1	304.42	4.0

\*1.5352g/l of dye; current = 99.87mA; these are examples of the results of many experiments.

Using Faraday's Laws and knowing the quantity of dye present, as well as the applied current, allowed the number of electrons involved in the reduction to be calculated. Examples of the values obtained are shown in Table 2 and illustrate that the reaction of Acid Red 88 is one involving four rather than two electrons. Thus reaction (iii) rather than reaction (iv) is the case.

Methyl Red (Figure 5b) was chosen as another dye for investigation. Its structure shows similarities to that of Acid Red 88 (Figure 5a), and thus it might be expected to undergo a reduction similar to that of Acid Red 88. During the experiments with Methyl Red it was assumed that it would undergo a four electron reduction, and latterly this was found to be true based upon a little spectroscopic evidence obtained at a later stage. Basically, several spectroscopic experiments were done to determine the purity of the impure Methyl Red, and they were found to confirm the electrochemical ones, in short indicating that the assumption of a four electron reduction was accurate. Table 3 shows the results of several experiments with Methyl Red. Its purity is quite low, but this is to be expected with some dyes through photolysis, salting-out procedures and general age.

In conclusion, a simple method and apparatus have been described for the determination of azo-groups, and hence certain azo-dyes. Unfortunately, the method cannot

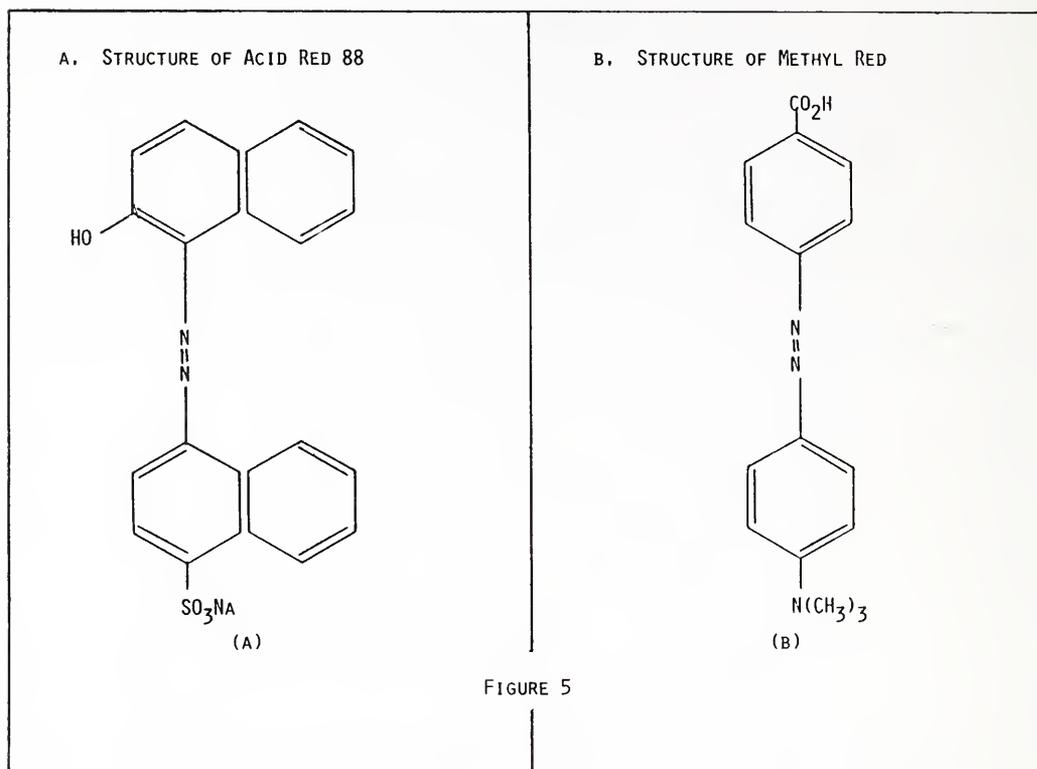


TABLE 3. Reduction of Methyl Red\*

mls of Dye	Time (secs)	Microeqs. Dye	Purity (%)
10.00	131.2	135.81	33.05
10.00	129.7	134.24	32.67
20.00	263.2	272.38	33.15
20.00	262.4	271.62	33.05

\*2.9378g/l of dye; assuming that it is a four electron reduction; these are examples of the results of many experiments.

be used with all azo-dyes owing to the possible presence of other reducible groups, for example nitro-groups. The unknown presence of these groups would be a major source of error, and even if their presence were known it would still present a problem unless a way to account for them were to be developed.

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