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RAPID ASSAY OF SOME AZO DYES USING SOLUTION THERMOCHEMISTRY

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Some azo dyes have been assayed using D. I. E. The analysis is completed in less than 1 minute with an average error of 1.05% at the 1 mMole level.The reagent used is titanium(III)chloride. Degassing of the solutions is not necessary.

Compared with presently available materials, the proposed procedure has the advantage of speed of assay over a fairly wide range of concentrations of the dyestuffs, the use of simple low cost equipment by semi-skilled personnel and a potential for automation.

Introduction

The industrial importance of azo dyestuffs is well known, it is essential that during and after their manufacture they can be assayed rapidly and economically. A rapid and low cost method which can cover a wide range of compounds at the various concentrations expected industrially and which can be automated is obviously desirable.

Samples which must be analysed include those obtained on-line during the preparation, the finished product and the non-recovered product which is allowed to go into the waste as an effluent. A routine method of assay which can cover the various concentrations of analyte likely to occur in these circumstances is required.

Among the methods used for the assay of industrial samples of dyestuffs are spectrophotometry and reduction of the azo group to the hydrazo group

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in a measured reaction generally using various inorganic reducing agents or polarographic methods.

Spectrophotometric methods involve a trace technique and thus industrial samples generally require major dilution of the original sample. They also suffer from the disadvantage that many of the impurities often encountered cause spectral interference.

Reductants such as hydrazine, using copper as a catalyst [1], lithium aluminium hydride [2] and other metal hydrides, including sodium borohydride, with palladised charcoal as a catalyst [3], tin(II) [4], iron(II) and titanium(III)chlorides [5] have all been used for the reduction of the azo groups of dyestuffs. The endpoints of such reactions may be followed by potentiometry or occasionally by visual methods but the very nature of the analyte often precludes the use of visual indicators.

Electrometric methods have the disadvantages that they are either trace methods (polarography) or the impurities in the industrial samples are often electroactive and give rise to erroneous results.

The advantages of methods of solution thermochemistry in the analysis of coloured samples and those containing electroactive impurities are well known. Many redox reactions have large heats of reaction suitable for use in solution thermochemistry and reactions such as indicated above offer potential for routine assay procedures.

Methods using Ti(III) have been widespread use and have been extensively investigated [6–8]. Some methods [7] require the solutions to be heated but all the methods used for the titanometric determination generally involve a titration and all the methods require the solutions used to be deoxygenated by de-gassing with a stream of nitrogen or carbon dioxide and the reagent used as the titrant must be stored and dispensed in oxygen-free conditions to prevent oxidation of the Ti(III) by dissolved and atmospheric oxygen during the course of the titration [5, 5a].

The use of titanium(III)chloride for the rapid determination of some industrial compounds containing nitro groups [9] indicated that the reagent could be used in a Direct Injection Enthalpimetric procedure.

This work reports the investigation of titanium(III) and other reductants including hydrazine, sodium borohydride and sodium dithionite which may be used to effect reduction of the azo group as reagents to be used for the rapid low cost assay of azo dyestuffs.

Experimental

Preliminary studies

Solutions of some selected dyestuffs were prepared from samples of the commercial dye-stuffs. These were dissolved in ethanol to give a saturated or near saturated solution and filtered from any residue. Water was added dropwise to the filtrate (or solution) until a precipitate was obtained and this was then redissolved and 'recrystallised' twice and air dried. For calibration purposes the samples so obtained were dissolved to known concentrations in aqueous ethanol. The composition of the solvent mixture for a particular dyestuff was determined experimentally.

Aliquots of the analytes in the insulated reaction vessel of the injection apparatus, which has been previously described [9] for the assay of nitrocompounds, were then reacted with the various reductants by injecting aliquots of these into the solutions which had been allowed to come to thermal equilibrium.

The enthalpimetric bridge and recorder system used have also been described [9].

Preliminary results

(a) Reduction with hydrazine

Although overall a significant heat of reaction was observed, the rate of attainment of equilibrium, even using a catalyst to speed up the reaction, was too slow to be of use in an enthalpimetric method. The curvature of the enthalpogram was too great for precise extrapolation.

(b) Reduction with sodium borohydride

Although the reaction is reasonably fast (visual observation), there was continuous evolution of gas, as a result of the hydrolysis of the borohydride and the heat of this reaction is much greater than that of the reduction. The latter cannot be precisely located on the recorder trace.

(c) Reduction with sodium dithionate

The reaction is too slow to be of analytical use in this procedure.

(d) Reduction with titanium(III)chloride

A useable enthalpogram was obtained.

Further work involved establishing the experimental parameters such as the optimum *pH* of the reaction medium, the type of buffer best suited to obtain this and the effects of dissolved oxygen on the heat pulses obtained.

Preparation of the titanium(III)chloride reagent, (approx. 0.5 M with respect to Ti(III))

This was prepared as previously described [9]. A known amount of the solid (ex-Aldrich Chemical Company) was dissolved in 1:1 HCl (11.5 M) and then diluted with freshly boiled distilled water to give a solution approximately 4 M w. r. t. HCl. The solution was stored under a hydrogen atmosphere by adding amalgamated zinc. The solution was left for 24 hours before use. The resulting solution showed a substantial heat of mixing when injected into blank solution of ethanol/water containing the proposed buffer. The heat of mixing was adjusted by adding urea or conc HCl (as appropriate) until the heat of mixing was practically zero.

Standardisation of the Ti(III) solution

Although an exact value for the molarity of the titanium(III) solution with respect to Ti(III) is not required for the enthalpimetric method, which is purely a comparative method, for the present study it was considered necessary to know the molarity of the titrant. The Ti(III) solution was thus assayed potentiometrically against Fe(III) solution of known molarity. The solution used had a molarity with respect to Ti(III) of 0.54 M.

Buffer solutions

Both potassium acetate [6] and potassium citrate [7] have been suggested for use at room temperature. Preliminary studies indicated that there was little difference between their efficacy, but since reagent grade potassium citrate is cheaper than the acetate, the citrate was chosen for this study. The buffer was prepared by using 10 ml of the potassium citrate and 1 ml of 0.2 M HCl per 50 ml of aqueous solution.

The effects of variation in the concentration of the citrate buffer in the titration of azobenzene (0.16 moles) was studied at concentrations between 0–30% w/v potassium citrate in the reaction medium.

With concentrations of the buffer solutions between 5–12.5% w/v, the reaction is too slow for use in a DIE method. Above 15% w/v the reaction is rapid and goes to completion in 1–2 sec.

There is an increase in the heat of mixing as the concentration of the citrate is increased. Thus to minimize this, the concentration of 15% w/v was chosen for all further work.

Effects of dissolved oxygen

Two series of aliquots of each of the dyestuffs in a buffered aqueous ethanol medium were reacted with the reductant.

In one series all the aliquots were de-gassed prior to titration, in the others the aliquots were used without any de-gassing.

Two methods of de-gassing the sample were studied. Samples were degassed by:

(i) passing a slow stream of oxygen-free nitrogen through the sample, dissolved in the aqueous ethanol, for 5–10 minutes.

(ii) de-gassing with carbon dioxide by adding approximately 0.1 g of sodium bicarbonate to the acidic buffer solution.

The degassing with nitrogen is preferred.

Table 1 Direct injection of titanum(III)chloride solution into dyestuffs with and without de-gassing of the sample solutions;
(a) Assay of azobenzene

Run No.	Pulse A	Pulse B
1	82.0	81.0
2	80.0	80.0
3	81.0	80.5
4	81.0	81.0
5	82.0	82.0
6	81.0	82.0
7	82.0	80.0
8	81.0	81.0
9	80.0	81.0
10	82.0	81.0
Mean	81.0	80.9

Amount used per aliquot = 0.16 millimole. Recorder sensitivity: –10 mV
F.S.D. Heat pulses obtained (measured in mm). Pulse A : with degassing*, Pulse B : without degassing
Standard deviation: without degassing = 0.72
with degassing = 0.78
*Degassing with a stream of N_2

(b) Assay of Methyl Orange

Run No.	Pulse A	Pulse B
1	101.0	102.0
2	99.5	100.0
3	100.5	99.5
4	99.0	101.0
5	100.0	99.5
6	99.0	101.0
7	99.5	101.0
8	101.5	100.0
9	98.5	101.0
10	100.0	101.0
Mean	99.85	100.6

Amount used per aliquot = 0.5 millimole. Recorder sensitivity: –50 mV
F.S.D. Bridge sensitivity adjusted to give approximately 100 divisions for the heat pulse of an aliquot. (See discussion). Pulse A: without degassing; Pulse B: with degassing*.
Standard deviation: without degassing = 0.94
with degassing = 0.81
*Degassing with a stream of N_2

The results for azobenzene (0.16 millimoles using an approximately 8 fold excess of titrant) and Methyl Orange (0.5 millimoles using an approximately 2.5 fold excess of titrant) titrated with titanium(III)chloride solution with and without de-gassing are shown in Table 1.

When using Methyl Orange, because of the increase in the amount of sample, it was necessary to adjust the sensitivity of the recorder to ensure that the trace remained on the chart. In order to ascertain the validity of the method as a routine method for assay, the sensitivity of the electronic bridge was also adjusted to give a peak height of approximately 100 divisions for the amount of sample used in the aliquot. (See discussion) When using Methyl Orange it was necessary to adjust the amount of the buffer solution to ensure complete solubility of the analyte (up to approximately 20% w/v buffer solution).

From the results it was concluded that the amount of oxidation of the titrant during the time of measurement was insignificant and therefore there was no need to de-gas the analyte/sample solution. All further work was done without de-gassing the sample solution.

Comparison of the DIE method and the potentiometric assay of the dyestuffs

A selection of the dyestuffs was titrated potentiometrically with Ti(III) solution. The results are given in Table 2.

Table 2 Comparison of the proposed method and a potentiometric method

Sample	Amount**	Method* (Error %)		
		A	B	C
	0.04	0.04 (0.00)	0.039 (2.5)	0.039 (2.5)
Metanil Yellow	0.08	0.079 (1.5)	0.08 (0.0)	0.081 (1.3)
	0.12	0.119 (0.8)	0.118 (1.6)	0.122 (1.6)
	0.04	0.039 (2.5)	0.037 (7.5)	0.04 (0.0)
Magneson I	0.06	0.59 (1.6)	0.06 (0.0)	0.061 (1.6)
	0.08	0.078 (2.5)	0.079 (1.25)	0.079 (1.25)
	0.02	0.02 (0.0)	0.019 (5.0)	0.02 (0.0)
Methyl Orange	0.04	0.039 (2.5)	0.038 (5.0)	0.039 (2.5)
	0.07	0.71 (1.4)	0.071 (1.4)	0.098 (2.0)

*Method (A): D.I.E. without degassing

*Method (B): D.I.E. with degassing

*Method (C): Potentiometric titration

**Amount: No. of millimoles of analyte in 10 ml of solution for assay.

(Each results recorded is the mean of four determinations on aliquots of the same solution.)

Method

The following dyestuffs were investigated:

(i) Metanil Yellow; 4-anilineazobenzene-m-sulphonic acid.

(ii) Magneson; C. I. Mordant Blue; 12; 5-chloro-2-hydroxy-3-(2-hydroxy-1-naphthylazo)-benzene sulphonic acid.

(iii) Magneson II; 4-(p-nitrophenylazo)-1-naphthol

(iv) Erichrome Blue Black; C. I. 15705

(v) Methyl Orange; C. I. 13025

(vi) Indigo Carmine; C. I. 73015; Indigo 5.5'disulphonic acid.

(vii) Arsenazo; C. I. 13010; 2(o-arsenophenylazo)-1,8dihyroxynaphthalne 3-6 disulphonic acid.

(viii) Orange II; (Acid Orange 7); 4-(2-hydroxy-1-naphthylazo)benzene sulphonic acid sodium salt.

(ix) 4-(2-pyridylazo)-resorcinol sodium salt; (NaPAR)
(x) Azo-violet; 4 nitrophenyl-(resorcinol)
(xi) Calmagite; 1-2(hydroxy-5-methyl-phenylazo)-2-naphthol-4-sulphonic acid.

Proposed procedure

Calibration

Prepare a stock solution (0.1 M) of the 'recrystallised' dyestuff in aqueous ethanol[*]. From the stock solution prepare a series of calibration solutions each 50 ml containing between 0–10 mMoles of the dyestuff, 10 ml of aqueous potassium citrate solution (15% w/v) and 1 ml of 0.2 M HCl. If precipitation occurs, add a further 5 ml of aqueous potassium citrate (15% w/v). Make up to volume with aqueous ethanol.

Pipette an aliquot (10 ml) of the calibration standard into the insulated reaction vessel of the titrator. Fill the submersible pipette to the mark with titanium (III) chloride solution which has been composed to give a zero heat of dilution. Rinse the outside of the pipette with distilled water and then dry it. Fit the polythene top carrying the pipette and the thermistor into the reaction vessel. Switch on the recorder and stirrer and stir the solution magnetically until thermal equilibrium is attained. (The recorder trace is parallel to the time axis.) Inject the titanium(III) solution into the sample. Record the heat pulse obtained.

Prepare a calibration graph of heat pulse against amount of dyestuff in the aliquot.

Assay of a dyestuff of known identity

Prepare a calibration curve using as the standard the recrystallised dyestuff. Prepare an assay sample of the dyestaff by dissolving a known weight of the sample (calculated to contain between 5–10 mMoles) in aqueous ethanol. Proceed as for the preparation of the calibration curve.

Adjust the sensitivity of the potentiometric recorder so that the heat pulse is within the range obtained for the calibration curve. From the heat pulse obtained determine the analyte content of the sample.

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[*] The composition of the aqueous ethanol depends upon the solubility of the analyte under assay and is ascertained by experiment.

Results and discussion

The dyes investigated have the same azo functionality as many of the typical dyes used industrially. All the dyestuffs investigated except Eriochrome Blue Black and Magneson II reacted under the chosen experimental conditions. It is considered that the method has sufficient potential to be regarded a suitable for routine assay in an industrial situation.

Since the actual molarity of the Ti(III) solution used was known, it was possible to calculate the amount of dyestuff that had reacted and ascertain if the reaction had gone to completion. The results are given in Table 2. From this table it may be seen that the proposed method is at least as reproducible as is the method involving de-gassing of the sample.

It is not possible to assume the dyestaffs are 100% pure, nor it is necessary to do so, since industrial samples are generally supplied on a comparative basis, i.e. a known concentration of the sample in a dye vat will provide an agreed amount of colouring matter. Assays are usually to determine whether a particular sample or batch of samples reaches the agreed specification. Since the proposed method is a 'comparison' method, once the calibration curve has been established for a selected dyestuff it is not necessary to standardise the titrant if fresh titrant is prepared since a variation of 10% in the concentration of the titrant will not result in any noticeable variation in the heat pulse. This means that the solutions can be prepared by semi-skilled workers at a lower economical cost.

Since the titrator uses a potentiometric recorder, with a stepwise voltage selector for sensitivity, it is possible to use the same method for any of the concentrations likely to be encountered in industry. If the titrant is made thermally neutral, viz: with a zero heat of mixing, then for a small concentration of analyte which results in a small heat of reactions, it is only necessary to adjust the sensitivity of the recorder to ensure that the heat pulse is within the calibration curve. Similarly for a concentrated sample which gives an 'off-scale' reading the sensitivity of the recorder may be suitably altered. In each case a simple calculation relates the concentration of the standard and recorder sensitivity used to prepare the curve and the sensitivity required to bring the heat pulse onto the curve and the actual concentration of the analyte:-

Conc. of sample = Apparent conc. from curve X (Sensitivity used for calibration/ (Sensitivity used for assay)

(where the sensitivity of recorder is the number of millivolts required for a full scale deflection (fsd.))

The proposed procedure is thus able to cover a wide range of concentrations. The use of at least a 2–3 fold excess of the reductant ensures that complete reduction occurs for most of the samples normally encountered. For solid samples it is necessary to prepare a solution within the normal working range.

For routine assay purposes, it is not necessary to prepare a calibration curve, comparison with a specification sample is sufficient.

Many industrial samples contain significant amounts of materials other than the analyte which are nontheless industrially acceptable since they do not affect the use for which the dyestuff is intended and in some cases are colour-inert substances included in the dye sample to enable standard recipes to be used in the dye vats.

In such circumstances it is only required to compare the analyte content of the sample with that of a 'specification standard'.

For such assay purposes the potentiometric recorder may be replaced with a digital voltmeter fitted with a shunt. Using the shunt, if the heat pulse from an aliquot of the 'specification standard' is electronically adjusted to give a reading on the millivoltmeter of, say, 100 mV, then subsequent assays of unknowns can be compared directly. For example a reading of 95 indicates that the sample has 95% of the analyte content of the specification sample.

Such a procedure is time and labour saving and thus reduces the overall cost of the assay.

The proposed procedure has the additional advantage that since no degassing of the solution is necessary the assay can be made automatic or semi-automatic. Thus the proposed method offers a rapid low cost method of assay which is analytically acceptable for industrial purposes.

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Zusammenfassung — Mittels DIE wurden einige Azofarbstoffe geprüft. Die Analyse wird in weniger als einer Minute mit einem mittleren Fehler von 1.05% für die Größenordnung 1mmol erstellt.
Gemessen an gegenwärtig erhältlichen Substanzen besteht der Vorteil der vorgeschlagenen Methode in der hohen Geschwindigkeit der Messung über einen großen Konzentrationsbereich der Farbstoffe, in der Anwendung einer einfachen und kostengünstigen Apparatur sowie in der Möglichkeit zur Automatisierung.