# Spectrophotometric determination of peroxydisulphate
# with *o*-dianisidine by flow injection

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*This paper is dedicated to Professor Ross Stewart on the occasion of his 65th birthday*

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Precise and accurate knowledge of peroxydisulfate ion concentration is critical in industrial polymer production, where it is extensively used as an activator. Its ability to oxidize in either acidic, neutral, or alkali media also makes it widely applicable in many other areas of chemistry.

In this paper we present an optimized spectrophotometric flow injection method for determination of peroxydisulfate. The analyte oxidizes *o*-dianisidine to form a stable product which has a convenient absorbance maximum at 450 nm. This provides a simple and sensitive alternative to present methods which are more costly, tedious, or complex.

*Key words*: spectrophotometric method, peroxydisulphate.

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Une connaissance exacte et précise de la concentration en ions peroxydisulfates est critique dans la production industrielle de polymères où il est utilisé d'une façon extensive comme activant. Comme il peut provoquer des oxydations en milieux acide, basique ou neutre, on peut l'utiliser dans plusieurs autres domaines de la chimie.

Dans ce travail, on présente une méthode spectrophotométrique optimisée pour déterminer la concentration en ion peroxydisulfate. Le produit à analyser oxyde l'*o*-dianisidine pour former un produit stable qui possède une bande d'absorption maximale à 450 nm. Cette procédure fournit une alternative simple et sensible aux méthodes actuelles qui sont plus couteuses, plus embêtantes ou plus complexes.

*Mots clés* : méthode spectrophotométrique, peroxydisulfate.

[Traduit par la revue]

## Introduction

The peroxydisulphate (persulphate) ion is a strong two-electron oxidizing agent

$$S_2O_8{}^{2-} + 2e^- \rightarrow 2SO_4{}^{2-}$$
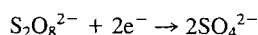
with a standard redox potential of $-2.01$ V in either neutral or alkaline solution (1). Its utility as an oxidizing agent for various substrates is derived from its ability to oxidize in acidic, neutral, and alkaline media (2). It has industrial importance as a polymerization activator, e.g., in production of polystyrene (3).

The literature provides a number of methods for the determination of persulphate. Kolthoff and Carr (4) reported several reductometric methods for the volumetric determination of persulphate ions. Of these, the iodometric and ferrometric (titrimetric) methods were the most practicable from the points of view of rate of reaction, accuracy, and simplicity (4). However, both procedures involve a back-titration step after the redox reactions with persulphate and thus are tedious to perform in any number. They also require reaction times of at least 15–30 min. Amin and Hareez (5) reported a procedure using a combination of titrimetry with alternating current (a.c.) polarography. This method is likewise tedious and complex. Amin (6) later reported an indirect amplification method by a.c. polarography which enabled measurement of persulphate concentrations as low as $2.6 \times 10^{-6}$ M with reasonable accuracy. This method, however, involves an extraction step followed by a back-titration. Ion-exchangers are also required to remove metal ions which form water-insoluble iodides that

would otherwise interfere. Kolthoff and Woods (7) reported an alternating-current polarographic method by which persulphate concentrations in the range $(10^{-4}–10^{-3}$ M) could be measured. This method was found to be highly temperature dependent. Substances that have wave potentials close to that of the iodate are known to interfere (6) (for example, Zn(II) in alkali media or Mo(IV), Cu(II), and Bi(II) under acidic conditions). These examples show that development of rapid selective methods for determination of persulphate has proven a difficult analytical problem.

The reaction between persulphate ions and aromatic amines, now known as the Boyland–Sims oxidation, was first reported in 1953 (8). A literature survey found that the reaction of persulphate with the substituted aromatic amine, *o*-dianisidine (ODA) has not previously been used for quantitative analysis of persulphate. However, persulphate ion has been used as a spray reagent for detection of aromatic amines and related compounds in thin layer chromatography (9), and the kinetics of the reaction of ODA with oxidizing agents such as $H_2O_2$ are well known (10, 11).

This paper reports the automated development of a simple flow injection procedure to determine persulphate ions at low concentrations, and is based on reaction with ODA. Flow injection (FI) is a versatile form of microflow analysis (12). Typical FI methods are fast, dependable, semi-automated, and use colorimetric or electrochemical detection in low volume flow-through cells. Samples are typically 30–100 μL in volume and throughput rates of 120 samples $h^{-1}$ are commonly reported.

Many manual procedures have been adapted to flow injection (12). Advantages of this include decreased reagent consumption and improved precision.

The present work has been carried out on an automated flow injection methods development system, which has been reported elsewhere (13). Such computer-controlled units have much to offer analytical chemistry. Reaction conditions may be specified from the keyboard and automatically adjusted. This is achieved by mixing streams of the required composition (reagent(s), solvent(s), buffer, diluent) using variable speed pumps and stock solutions. Sample introduction is via computer-controlled injection valves or stream switching valves. Optimization of such systems requires that operating conditions be found which maximize some measure of performance (e.g. extent of reaction) whilst limiting unnecessary sample dispersion. This is typically a highly multivariate problem, as flow conditions must be optimized in addition to the chemical parameters.

Simplex optimization (14–16) and automated response surface mapping (13, 17) have been implemented on these systems. The former provides a rapid means to find the optimum conditions for analysis. The latter seeks to establish the effects of system variables such as flow rates, sample size, pH, and ionic strength. Together or separately these facilitate essentially operator-unassisted methods development, in a matter of a few hours.

## Experimental

### Reagents

A stock solution of persulphate ($1.00 \times 10^{-2}$ M) was prepared by dissolving 0.676 g of potassium persulphate (Fisher Scientific, Fairlawn, NJ), in 250 mL of distilled water. Standard solutions were prepared from this by appropriate dilution. A $1.0 \times 10^{-2}$ M ODA solution ($2.443$ g L$^{-1}$) (Aldrich, Milwaukee, WI) was freshly prepared daily in a 40% v/v mixture of acetone in water. Solutions of ODA were freshly prepared every day. A buffer solution was prepared from 100 mL of 0.1 M 3,3-dimethylglutaric acid (Aldrich, Milwaukee, WI) in 1 M sodium chloride (18). Sodium chloride was present to minimize the effect of changes in ionic strength of the reaction media. Various reaction pHs for the batch method experiments were obtained by adding appropriate volumes of 0.1 M sodium hydroxide to the buffer.

### Apparatus

The automated flow injection analyzer used was the same as in previous methods development (16, 17) and is discussed in detail elsewhere (13). The options used in this work included a custom-built variable speed peristaltic pump unit containing five independent pump heads, a high precision variable speed peristaltic pump (Models C-4V or C-6V, Alitea USA, Seattle, WA), and a six-port air-driven solenoid-actuated injection valve (Rheodyne 5020P, Cotati, CA) equipped with a 100 μL sample loop. A diode array spectrophotometer (Hewlett Packard 8452A) with a standard 1 cm quartz cell was used for absorption measurements. This was interfaced to the control computer, an IBM PC/AT compatible computer (NORA Systems, Vancouver, B.C.), via an IEEE-488 instrumentation interface. All the other units were controlled by the same microcomputer as described elsewhere (13). For the flow injection studies, a 30 μL, 1 cm path length quartz flow cell was used. The pH of reaction mixtures was determined on-line using a flow through electrode cell, a Ag/AgCl electrode (Radiometer America Electrodes Inc., GK473901), and a laboratory pH meter (Model 119, Fisher Scientific, Richmond, B.C.). Polytetrafluoroethylene (PTFE) tubing of 0.5 mm i.d. was used throughout. Software was written in Microsoft QuickBASIC$^R$ version 4.0, as was the code used for nonlinear curve fitting and other data processing tasks. The optimization algorithm used was the composite modified simplex method (14, 19, 20). Response surface plots were generated using a commercial scientific graphics program (SURFER$^R$ v. 3.0, Golden Software, Golden, CO).
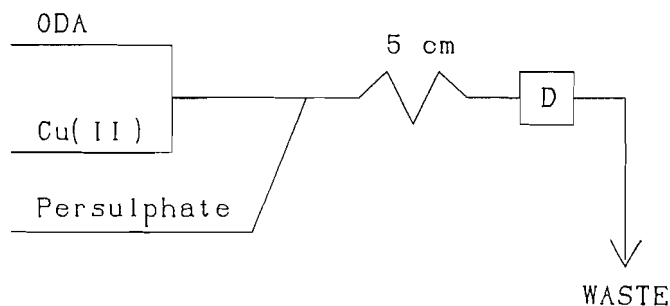


FIG. 1. Continuous flow manifold used for stopped flow kinetic studies for the reaction between ODA and persulphate. The reagent stream was of ODA in 40% v/v acetone in DMGA buffer at pH 7.0. A $1.0 \times 10^{-4}$ M Cu(II) stream was used to catalyze the reaction. Absorbance measurements were made using the spectrophotometer, D.

### Procedures

#### Batch kinetics studies

A series of preliminary batch kinetics experiments were performed to investigate the suitability of ODA as a reagent for the determination of persulphate ions.

A standard reaction was first obtained by adding 5.0 mL of $1.0 \times 10^{-4}$ M persulphate solution to a mixture containing 5.0 mL of $1.0 \times 10^{-2}$ M ODA solution and 10.0 mL distilled water. After thorough mixing an appropriate reaction mixture volume was transferred to a standard 1 cm cell in the spectrophotometer. Absorbance measurements at 450 nm were initiated 30 s after the start of the reaction and acquired at 10 s intervals for a period of 900 s. The effect of pH on this reaction for the above ODA concentration was then established by adding 10.0 mL of buffer solution at a known pH in place of the distilled water. The pH was varied from 3.00 to 9.00.

#### Stopped flow kinetic studies

Once the optimum reaction pH was identified, stopped-flow experiments were conducted to determine the kinetic parameters (i.e. final amount of product formed, order of reaction, and rate constant, $K'$). The flow configuration used for the stopped flow experiments is as shown in Fig. 1. A single Alitea pump was run at maximum speed to merge the reagents and then rapidly transport the reaction mixture to the cell (in less than ½ s from the tee to observation window). The flow was then stopped and absorbance measurements were made at 1 s intervals at 450 nm for a period of 400 s.

The effect of various metal ions on the kinetics at pH 7 was then established by adding dilute metal ion solutions in place of the 10.0 mL distilled water. A similar procedure was followed using neutral salts to determine the effect of ionic strength on the reaction. Finally, the effect of other possible solvents and solvent mixture composition on the ODA solution and product stability was determined.

#### Flow injection studies

The flow injection configuration used for both the automated simplex optimization and response surface mapping studies is shown in Fig. 2a. The reagent stream, R, consisted of ODA merged with distilled water to give a total flow rate of 1.00 mL min$^{-1}$ and maximum ODA concentration of $1.0 \times 10^{-2}$ M. The buffer stream, B, comprised 0.10 M 3,3-dimethylglutaric acid in 0.10 M NaCl merged with a 0.10 M sodium hydroxide stream to give a total flow rate of 1.0 mL min$^{-1}$ and a maximum NaOH concentration of 0.10 M. The carrier stream was made up of $5.00 \times 10^{-4}$ M Cu(II) solution as a catalyst, flowing at a fixed rate of 2.00 mL min$^{-1}$. By allowing the NaOH flow rate to vary from (0.00–1.00) mL min$^{-1}$, the pH was varied from about 3.50–10.00. The flow at the detector was kept at a constant total rate of 3.00 mL min$^{-1}$. This ensured a constant sample residence time in the system. Separate pumps were used for each solution. The internal diameter (i.d.) of reaction coils was 0.5 mm for all sets of experimental conditions. Before any sample injection was made, the system was allowed to equilibrate to a steady baseline reading.
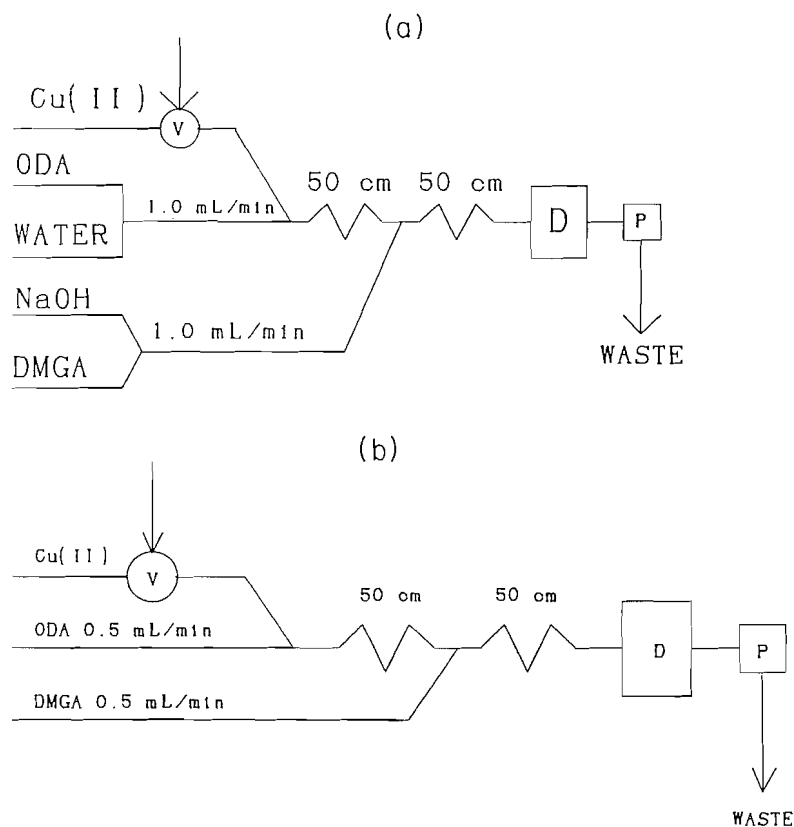
(a)



(b)



FIG. 2. (a) Flow injection manifold used for automated optimization and response surface mapping studies. This comprised a $5.0 \times 10^{-4}$ M Cu(II) carrier stream flowing at a constant flow rate of 2.0 mL min$^{-1}$, an injection valve with 100 μL loop (V), reagent and water streams buddied at 1.0 mL min$^{-1}$, a buffer stream consisting of NaOH and DMGA buddied at 1.0 mL min$^{-1}$, a spectrophotometer (D), and a pH electrode cell (P). (b) Flow injection manifold used for the calibration studies and investigation of the effect of organic substances. This is comprised of a $5.0 \times 10^{-4}$ M Cu(II) carrier stream flowing at a constant flow rate of 1.5 mL min$^{-1}$, an injection valve with 100 μL loop (V), an $1.0 \times 10^{-2}$ M ODA reagent stream flowing at 0.5 mL min$^{-1}$, a DMGA buffer stream at pH 7.0 flowing at a constant 0.5 mL min$^{-1}$, a spectrophotometer (D), and a pH electrode cell (P).

TABLE 1. The response, pH, and the relative standard deviation (RSD) of the initial (expt. #1) and the five best simplex experimental conditions (total number of experimental points, 20)

| Expt. # | Variable #1 (ODA)/mL min$^{-1}$ | Variable #2 NaOH/mL min$^{-1}$ | Response[a] | pH | (RSD)/% |
|---|---|---|---|---|---|
| 1 | 0.400 | 0.400 | 0.071 | 4.42 | 1.5 |
| 4 | 0.840 | 0.672 | 0.198 | 5.75 | 0.3 |
| 5 | 1.000 | 0.807 | 0.198 | 7.5 | 1.6 |
| 7 | 1.000 | 0.664 | 0.211 | 6.67 | 0.7 |
| 8 | 0.763 | 0.775 | 0.190 | 7.12 | 1.0 |
| 12 | 1.000 | 0.585 | 0.189 | 5.26 | 0.6 |

[a]Responses were measured as peak absorbance.

A 100 μL sample of $1.00 \times 10^{-4}$ M persulphate was then injected into the carrier stream and absorbances measured at 450 nm. The pH of the reaction mixture was measured simultaneously in a simple-flow through cell placed 5 cm after the spectrophotometric detector.

*Automated simplex optimization*

During automated simplex optimization, the flow rates of all streams save for the carrier stream were automatically adjusted. This was to determine the optimum flow rates for the reagent and NaOH streams (optimum pH from flow rate of NaOH and the buffer stream).

The initial experimental conditions and the best experimental conditions established during the simplex optimization procedure are summarized in Table 1. The best conditions obtained correspond to those of experimental point number 7, i.e. ODA and NaOH flow rates

of 1.00 and 0.66 mL min$^{-1}$ respectively, with the pH of the reaction mixture equal to 6.67 as recorded by the pH meter.

Once the optimum conditions were established, these were implemented on a simpler flow injection system shown in Fig. 2b, comprising two pumps, three pump tubes, and a single injection valve. This was used for subsequent routine analysis, calibration, and studies on the effect of organic substances. Alternatively, a single pump could have been employed with the carrier stream channel having a pump tubing which could provide a flow rate that is three times higher than that of the other channels.

*Automated response surface mapping*

A more thorough investigation of the ODA–persulphate response surface was then achieved by carrying out triplicate experiments at
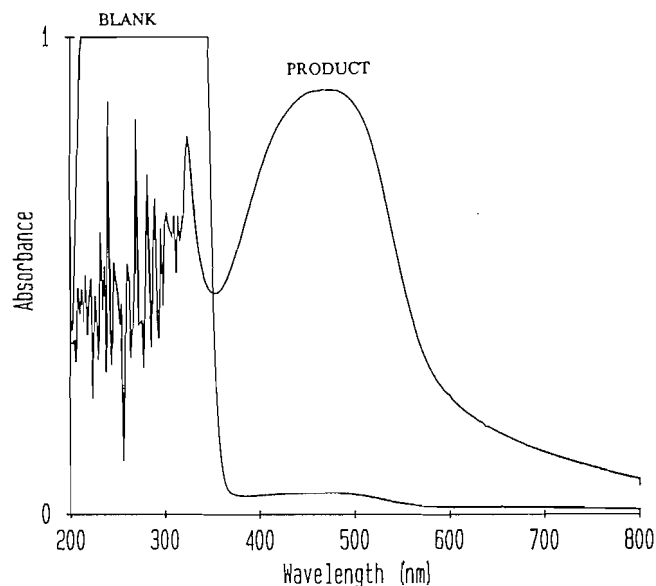
FIG. 3. UV–visible absorption spectra of the ODA–persulphate reaction product: (*1*) reagent blank with water as reference; (*2*) ODA–persulphate mixture after 300 s with the reagent blank as reference.

TABLE 2. Effect of metal ions on the ODA–persulphate reaction; absorbance measurements taken 5 min after initiation

| $M^{n+}$ | $[M^{n+}]/mol\,L^{-1}$ | Absorbance | Enhancement factor[a] |
|---|---|---|---|
| Blank | — | 0.747 | 0.63 (300 s) |
| $Mo^{6+}$ | $1 \times 10^{-3}$ | 0.779 | 0.66 (300 s) |
| $Mn^{2+}$ | $1 \times 10^{-3}$ | 0.946 | 0.80 (300 s) |
| $Ni^{2+}$ | $1 \times 10^{-3}$ | 1.040 | 0.88 (215 s) |
| $Co^{2+}$ | $1 \times 10^{-3}$ | 1.038 | 0.88 (200 s) |
| $Zn^{2+}$ | $1 \times 10^{-3}$ | 1.108 | 0.94 (245 s) |
| $Pb^{2+}$ | $1 \times 10^{-3}$ | 1.133 | 0.96 (245 s) |
| $Cu^{2+}$ | $1 \times 10^{-3}$ | 1.181 | 1.00 (85 s) |
| $Fe^{3+}$ | $1 \times 10^{-3}$ | Interferes | — |
| $Ag^+$ | $1 \times 10^{-3}$ | Interferes | — |

[a]Enhancement factor is calculated relative to $10^{-3}$ M $Cu^{2+}$ ions and the values in brackets show the times at which maximum absorbance were recorded with $[ODA] = 5.0 \times 10^{-3}$ M, $[S_2O_8^{2-}] = 1.0 \times 10^{-4}$ M, buffered at pH = 7.0.

each of the 64 sets of reaction conditions. These were regularly spaced across the search space in the pattern of an $8 \times 8$ square lattice. The average absorbance at each set of conditions was taken as the height of the response surface at that point.

## Results and discussion

### Selection of analytical wavelength

The absorption spectra of $5.0 \times 10^{-3}$ M ODA in 40% v/v acetone–water mixture and that of the reaction product formed from the reaction between $5.0 \times 10^{-3}$ M ODA in 40% v/v aqueous acetone and $1.0 \times 10^{-4}$ M persulphate after 5 min as reaction time are shown in Fig. 3. This reveals that absorbance measurements due to formation of product can be made at 450 nm without interference from the reagent matrix.

### Batch kinetic studies

#### Effect of metal ions

A number of metal ions are known to catalyze reactions involving persulphate ions. The metal ions studied are given in Table 2. Most showed catalytic activity to varying degrees.

TABLE 3. Effect of neutral salts on rate of formation of product; reaction conditions: $[ODA] = 1.0 \times 10^{-3}$ M, $[S_2O_8^{2-}] = 5.0 \times 10^{-5}$ M

| Salt | Concentration mol $L^{-1}$ | Absorbance after 600 s | Relative increase (%) |
|---|---|---|---|
| Blank | 0.0 | 0.0932 | 0 |
| NaCl | $1.0 \times 10^{-4}$ | 0.1479 | 58.69 |
| | $4.0 \times 10^{-3}$ | 0.1488 | 59.66 |
| KCl | $1.0 \times 10^{-4}$ | 0.1401 | 50.32 |
| | $4.0 \times 10^{-3}$ | 0.1495 | 60.41 |
| $KNO_3$ | $1.0 \times 10^{-4}$ | 0.1040 | 11.59 |
| | $4.0 \times 10^{-3}$ | 0.1323 | 41.95 |

Both Fe(II) and Cu(II) showed remarkable catalytic activity even at concentrations as low as $10^{-5}$ M. Reactions catalyzed by Fe(II), however, yielded very unstable products. This was not surprising since the reaction mechanism is thought to be via a free radical species (4) producing Fe(III), which in itself formed a colored complex with ODA. A substantial catalytic effect was also observed for Pb(II). The catalytic activities of Mn(II), Co(III), Ni(II), Zn(II), and Mo(VI) were much less than that of Cu(II). About a 100-fold concentration ($10^{-1}$ M) of these metal ions had a comparable catalytic effect as that of the Cu(II) ($10^{-3}$ M). Both Ag(I) and Fe(III) formed colored complexes with ODA and thus interfered.

Further investigation of the suitability of Cu(II) as a catalyst in the ODA–persulphate reaction was then performed. The concentration of Cu(II) was varied from $10^{-7}$ to $10^{-1}$ M. At concentrations below $10^{-6}$ M, the reaction rate was slightly increased relative to the uncatalyzed reaction. For concentrations between $10^{-6}$ and $10^{-4}$ M, equilibrium of the reaction mixture was reached between 240 and 90 s, respectively, while with concentrations between $5.0 \times 10^{-4}$ and $10^{-1}$ M, equilibrium was attained within 60 s. A Cu(II) concentration in the range $10^{-3}$ to $10^{-2}$ M is recommended. This is a compromise between the rate of attaining equilibrium and product instability, since at concentrations above $10^{-2}$ M Cu(II) instability became more apparent.

### Effect of neutral salts

Ionic strength often varies from sample to sample and so the effects of NaCl, KCl, and $KNO_3$ concentrations on the ODA–persulphate reaction was investigated. Table 3 summarizes the effect of various concentrations of these neutral salts on the rate of reaction. The reported absorbances were measured 300 s after initiating the reactions. All these neutral salts showed a positive effect on the rate of the reaction with increase in concentration. KCl and NaCl showed approximately equal effects which were greater than that observed with $KNO_3$ (Table 3).

### Effect of % v/v composition of acetone in water as solvent

The % v/v composition of acetone in water was varied from 20 to 100%. The lower limit was chosen because of the limited solubility of ODA in water. The results showed a general increase in rate of the reaction with increase in mole fraction of acetone, but product stability decreased. In the presence of $10^{-4}$ M Cu(II) as catalyst, equilibrium was attained in less than 60 s with compositions above 40%. Product stability, however, decreased with increase in % composition above 40%. Under similar conditions with 20–40% acetone, equilibrium was achieved between 60 and 90 s, respectively, with product stability times greater than 300 s (product stability times = time
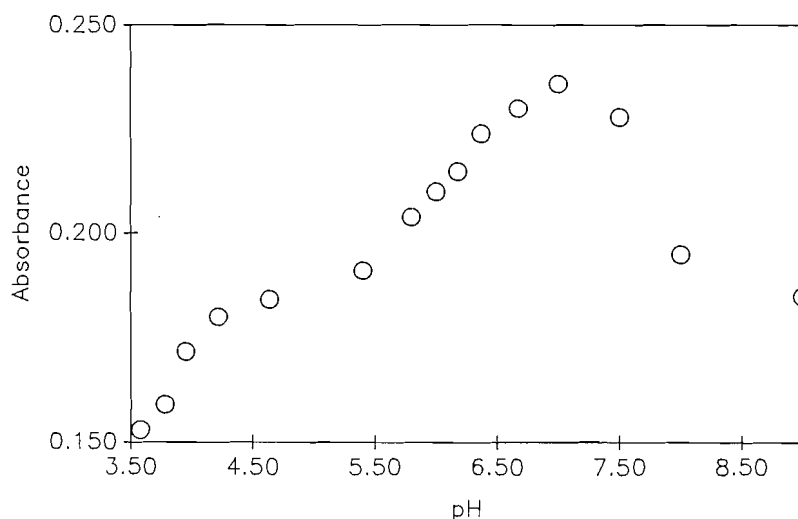
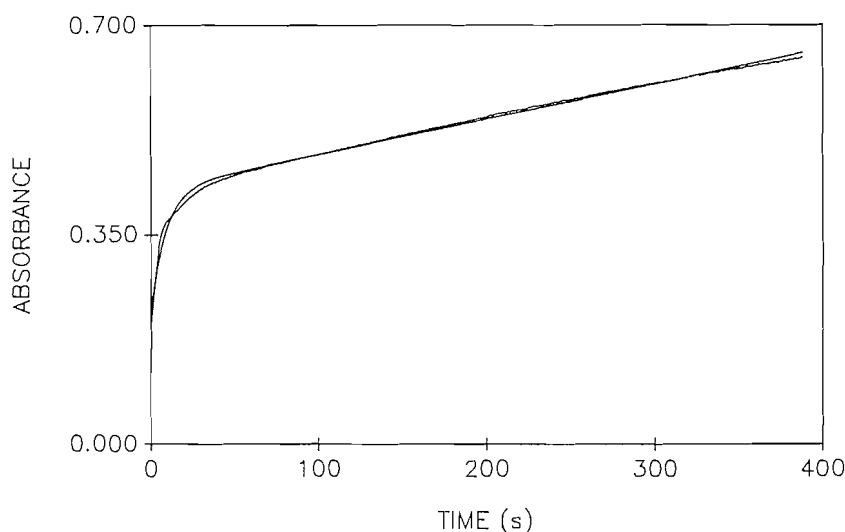FIG. 4. Absorbance at 450 nm for the ODA–persulphate reaction mixture as a function of pH.



FIG. 5. Fit of a pseudo-first order reaction model to data collected for the reaction between ODA and persulphate at pH 7.0.

period over which absorbance readings were recorded within ±0.05 absorbance units). Thus a composition of between 20 and 40% is recommended.

### Effect of reaction mixture pH

3,3-Dimethylglutaric acid (0.1 M) in 1 M NaCl and 0.1 M NaOH was used to vary the pH of the reaction mixtures from 3.5 to 10.0. A high concentration of NaCl was employed to keep the ionic strength of reaction medium constant. Figure 4 shows the responses obtained from reaction mixtures at various pH values. Absorbance was measured after 300 s of reaction time. From these batch reactions, the maximum response obtained corresponded to neutral conditions; however, acceptable sensitivity was obtained between pH 6.5 and 7.5.

### Reaction kinetics studies

Reaction kinetics were investigated at neutral pH conditions under pseudo-first order conditions, with ODA in excess. Expressing the reaction as

$$S_2O_8^{2-} + n\text{ODA} \rightarrow \text{Product}$$

the reaction rate can be written as

$$\text{Rate} = K'[S_2O_8^{2-}]$$

where $K'$ is the pseudo-first order rate constant.

A non-linear curve fitting program was used to extract the pseudo-first rate constant from the stopped-flow experimental data. The equation fit to the data was

$$A_t = A_0[1 - \exp(-K't)] + C$$

where $A_t$ is the absorbance at time $t$, $A_0$ is the final solution absorbance due to product, and $C$ is a constant background term. The flow through cell was thermostated at 25°C. Figure 5 is representative of the fits of the model to the data. Excellent fits were obtained for each of the solutions tested. The pseudo-first order rate constant obtained from the fitting routine was 0.06 ± 0.01 s⁻¹. The final equilibrium absorbance due to the product remained unchanged within ±0.01 absorbance units for ODA concentrations in the range 0.001 to 0.01 M, an indication that reaction was going to completion. The reaction is essentially finished in less than 90 s.
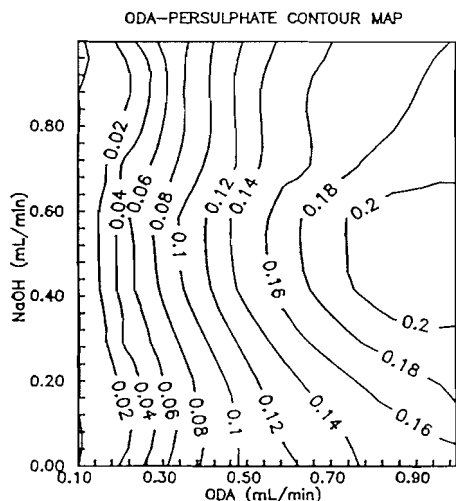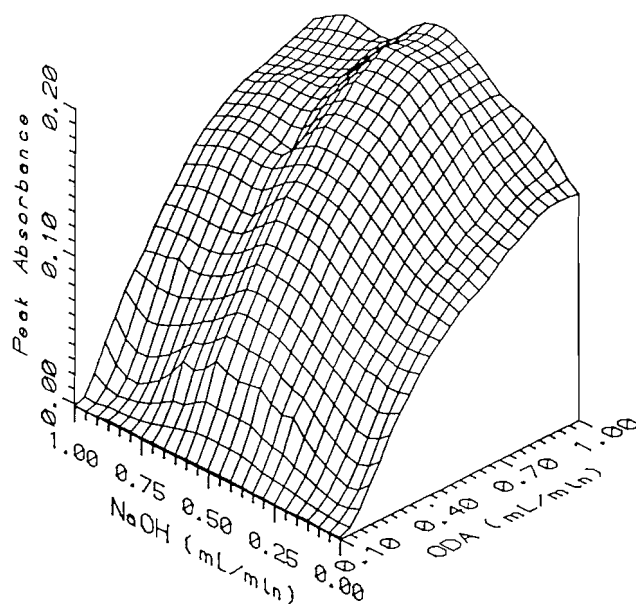
FIG. 6. The ODA–persulphate response surface shown as a 3D plot and its corresponding contour map. The response shown is the peak absorbance at 450 nm. ODA and NaOH flow rates are in mL min$^{-1}$.

TABLE 4. Optimization of coil length for ODA–$S_2O_8^{2-}$ reaction

| Coil length/cm | Peak maximum (AU) | Relative performance (%) |
|---|---|---|
| 55 | 0.391 | 77.4 |
| 60 | 0.423 | 83.8 |
| 80 | 0.466 | 92.3 |
| 90 | 0.477 | 94.5 |
| 100 | 0.505 | 100 |
| 110 | 0.477 | 94.5 |
| 120 | 0.446 | 88.3 |

simplex optimization was 2.0 h. This was for about 20 sets of experimental conditions. For the automated response surface mapping, a factorial design consisting of 64 experiments each with three replicates, was used. This optimization process took about 4 h.

The results of the response surface mapping study are shown in Fig. 6. The ideal pH for this reaction was established as 7.0, however the pH range 6.0 to 7.5 could be used without great loss in sensitivity. This range corresponded to NaOH stream flow rates in the range 0.30–0.80 mL min$^{-1}$ for the FIA manifold of Fig. 2a. Thus the whole pH range 6.0–7.5 is recommended. These results were in good agreement with those from the simplex optimization procedure. As shown in Table 1, the optimum flow rate conditions obtained from simplex experiments fall in the region considered optimum from the response surface studies. Also the pH's corresponding to the five best simplex experimental conditions are within the pH range established as optimum from the response surface studies. The optimum conditions established by the simplex procedure were thus confirmed by the automated response surface mapping studies at the expense of more experiments and somewhat less information about the region of the optimum.

The effect of reaction coil length on the sensitivity of the system was determined by performing 10 replicate experiments under the optimum conditions obtained from the first simplex optimization experiment with different reaction coil lengths. A 100 cm coil length was established as optimum. Results of these studies are summarized in Table 4. Since this value was (fortuitously) as used in the previous automated chemical flow optimization, no further optimization experiments were warranted. The automated analyzer used does not presently have the capability of automatically adjusting coil length.

## Automated optimization of the flow injection system

Both simplex optimization and response surface mapping were employed. The results are compared. Simplex optimization was chosen as an optimization procedure because it rapidly optimizes chemical and flow conditions in flow injection systems (12). While this approach adequately locates the maximum, it gives little information about the global nature of the response surface (13). Some workers have advocated carrying out an additional set of experiments around the best conditions found by an experimental optimization to confirm that the true optimum has indeed been located and establish the effect of changes in experimental variables in this region (21). This provides the experimentalist with evidence of the stability and therefore experimental repeatability of the analytical method. This was not done here as the same function was achieved globally by the response surface mapping experiments.

With three replicate runs at every experimental condition, the total time taken to achieve the optimum conditions by

## Interference studies

In polymerization studies with persulphate as activator, persulphate must often be determined in the presence of various organic substances. Thus the effect of methanol, ethanol, allyl acetate, formaldehyde, ethyl acetate, and allyl alcohol on the ODA–persulphate reaction was investigated. Of these substances, methanol and ethanol showed the least effect even at concentrations as high as 1.0 M. Solutions containing 2.5 M methanol and 1.0 M ethanol caused an error of about +0.22% in the determination of 2.0 × 10$^{-4}$ M persulphate ions. At 0.25 M concentrations of both allyl alcohol and allyl acetate errors of +0.50% and −6.98% respectively were recorded. The worst acceptable interference was obtained with 0.5 M ethyl acetate which gave an error of +11.80. Reaction in the presence of formaldehyde resulted in a turbid mixture which then formed a pinkly colored precipitate. Formaldehyde thus strongly interferes, and should not be present.
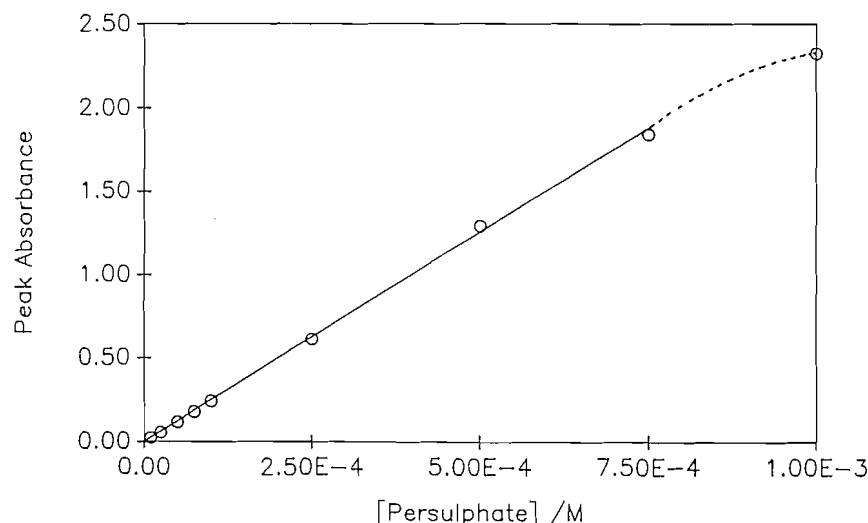
FIG. 7. Calibration curve for developed method of persulphate determination. The solid line represents the linear dynamic range.

### Analytical implications

The calibration curve obtained with the flow geometry of Fig. 2b is shown in Fig. 7. This indicates a linear dynamic range of $2.50 \times 10^{-5}$ M to $7.5 \times 10^{-4}$ M, with a sensitivity of $2.4 \times 10^3$ Abs $M^{-1}$. The detection limit ($3 \times$ standard deviation of the baseline noise) with this system was $5.0 \times 10^{-7}$ M. The lower limit of the linear dynamic range was detected with a relative standard deviation of 1.5% from 10 replicates.

### Conclusions

The analytical method developed is both simple and sensitive. Other advantages generic to flow injection techniques include high precission, high sample throughput rate, and low sample and reagent consumption rates. Together these give the analytical procedure reported here many advantages over previous classical (4, 9), titrimetric (4), and the polarographic methods (6, 7). While a few organic species and metal ions do interfere, either the extent of their effects is tolerable, or the interference is usually obvious in the reaction mixture.

### Acknowledgements

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