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Shapes of Normal and Reverse Flow Injection Signals: On-line Formation of Iodine From Iodate, Iodide and Hydrogen Ion With Detection by Visible Spectrophotometry

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Signal shapes for the on-line formation of iodine from iodate, iodide and hydrogen ion in a single-channel manifold using large-volume slug and large-volume time-based injections have been determined using visible spectrophotometry. These large injection volume studies were made first as a means of understanding the shapes of normal and reverse flow injection signals obtained at more conventional injection volumes (10–100 μl). The signal shapes at large injection volumes were determined for the six possible combinations of the reagents in the two solutions serving as carrier stream and injectate so that one solution contained two reagents and the other solution one or two reagents. Each combination of reagents represents two complementary systems in which the roles of each solution as carrier stream and injectate are reversed. At these large injection volumes each signal consisted of two independent peaks caused by dispersion at the front and rear boundaries of the injected bolus. The signals obtained for the time-based injections for complementary systems were identical in shape and height except that the front peak of one system was identical with the rear peak of its complementary system and *vice versa*. Clearly, at such large injection volumes the terms normal flow injection (nFI) and reverse flow injection (rFI) have no real meaning, the shape of each independent peak being determined by the composition and relative positions of the two solutions forming the boundary at which the peak is formed. For slug injections, similar shapes were observed but the peak heights were affected markedly by the greater dispersion at the rear boundary which travels further than the front boundary. This comparison of the signals obtained with slug and time-based injections, despite different flow-rates being used for the two modes of injection, clearly shows the effect of the unequal dispersion at the two boundaries in the slug injection method. Examination of the signals obtained with time-based injection, however, clearly indicates that the solution compositions, and their relative positions in the flow stream, also affect the shapes and relative heights of the front and rear peaks. The shapes of all these signals are illustrated. The effect of reducing the slug injection volume stepwise from 2 ml to 100 μl was studied for the IO_3^-–I^- < H^+ and H^+ < IO_3^-–I^- systems (< denotes the direction of the boundary shape). This indicated that the shapes and heights of the single peaks observed in the rFI and nFI formation of iodine carried out at the more conventional lower injection volumes are determined by dispersion at the rear and front boundaries of the bolus, respectively. Hence, as the two peaks observed in a large-volume injection merged as the injection volume was decreased, the major peak predominated and became the observed signal. The use of a much smaller injection volume was necessary in rFI than in nFI in order to obtain a single peak.

Keywords: *Flow injection; reverse flow injection; visible spectrophotometry; iodine formation; signal shape*

Reverse flow injection (rFI) used with a single-channel manifold differs from normal flow injection (nFI) in that, in rFI, the reagent is injected into a sample carrier stream instead of the sample solution being injected into a reagent carrier stream. Johnson and Petty[1] were the first to use the term rFI and to use rFI in this way. They determined phosphate by injecting a molybdate reagent into a sample carrier stream and monitoring the 12-molybdophosphate formed by visible spectrophotometry. The rFI method was found to be about five times more sensitive than the nFI method because phosphate is determined with very little dilution in rFI. Fogg and co-workers have described reverse flow injection amperometric methods for the determination of phosphate and nitrite,[2] and indirect methods were developed for the determination of aromatic amines, phenols and sulphite based on rFI formation of nitrosyl bromide,[3] bromine[4] and iodine.[5]

It was pointed out that the shape of rFI signals would not be expected to be the same as that of nFI signals,[6] and this was demonstrated by using an amperometric method for determining sulphite in which iodine was formed on-line in the rFI manner and reacted with sulphite sample dispersing in the nFI manner.[5] In nFI the sample disperses continuously after injection. In rFI the sample is, in effect, present in infinite supply in the carrier stream. When dispersion begins, the equivalent sample concentration at the extremities of the bolus rapidly reaches that in the carrier stream and if the chemical reaction is rapid this sample is converted fully into monitorand. Eventually, with sufficient dispersion and a sufficiently small injection volume, the equivalent sample concentration throughout the reagent bolus will approach that in the reagent stream. Whether this sample is converted completely into monitorand, however, depends on whether the reagent concentration remains at a sufficiently high concentration despite its dispersion. Clearly, the reagent is injected at as high a concentration as possible but it is diluted rapidly during its dispersion in the nFI manner and its concentration may become limiting eventually.

If the determinand is fully formed throughout the reagent bolus under conditions of high dispersion, the signal might be expected to be rectangular in shape, *i.e.*, a steep-sided flat-topped peak. With slightly less dispersion, whereas the equivalent determinand concentration at the extremities of the bolus will be very close to that in the carrier stream, in the centre of the bolus it will be lower. Hence the predicted shape at this dispersion is a hollow-topped rather than a flat-topped peak. At even lower dispersions a double peak would be expected. If dispersion were the same at the front and rear

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edges of the bolus these double peaks might be expected to be of equal height. Our previous amperometric work[5] indicated that this is not the case, however; the rear peak is appreciably higher than the front peak (see Fig. 3 in reference 5).

In the present work the iodate - iodide - acid system was studied using visible spectrophotometric detection of iodine in order to examine further the shape of these rFI signals and to compare them with nFI signals. At large injection volumes, when the carrier stream does not reach the centre of the bolus, the terms nFI and rFI can be considered to lose their significance. Under these conditions each signal obtained corresponds to dispersion across two completely independent boundaries and consists of two independent peaks. These large injection volume studies were made first as a means of understanding the shapes of normal and reverse flow injection signals obtained at more conventional injection volumes (10–100 μl).

Experimental

Single-channel manifolds incorporating six-port rotary valves were used throughout. In the manifold used for performing slug injections the loop was filled by drawing injectate through it by means of an auxiliary pump. The manifold used for performing the time-based non-loop injections is shown in Fig. 1. On switching the valve, injectate is drawn through the detector in place of the carrier stream. The volume "injected" is determined by the length of time that the valve remains in this position before it is switched back to its original position. Time-based injections were performed under computer control. The computer system used was that described by Stone and Tyson.[7] The injection valve was automated by means of a stepper motor and reduction gear drive (McLennan Servo Supplies), controlled by a dedicated microprocessor unit. This could be programmed to give any desired switching sequence, with a timing accuracy of 0.1 ms and precisions for replicate injections of better than 1% relative standard deviation (RSD). In that work,[7] time-based injections were performed with the aid of a large-volume sample loop. The disadvantage of that system is that there is a momentary change of flow-rate when the sample loop is switched into the line. In the present work, time-based injections were not performed via a sample loop and hence the problem was avoided. The transmission tubing was made of PTFE, length 3 m, 0.8 mm i.d. Ismatec Reglo pumps were used and the detector was a Pye Unicam SP-6-250 visible spectrophotometer fitted with a 10-mm path length, 8-μl quartz flow cell. Iodine was monitored at 352 nm.

Results and Discussion

Large-volume (2 ml) Injections

Initial experiments were carried out using large-volume (2 ml) injections in order to be able to study the signal shapes at each boundary of the bolus without interference from dispersion at the other boundary. We expected to find that the difference in the heights of the double peaks observed previously using amperometric detection when acid was injected into an iodate - iodine carrier stream was caused by the rear boundary of the bolus having to travel further than the front boundary. Essentially, if the length of the transmission tube is L and the length of the sample loop is l, the front boundary in the slug injection travels a distance L, whereas the rear boundary travels a distance $L + l$ and will be dispersed more. In time-based injections a new rear boundary is created, which travels the same distance (L) as the front boundary to the detector. When time-based injection was used here, however, although an appreciable effect on the actual and relative sizes of the twin-peak signals was observed, the two peaks were not of equal size and clearly other significant factors were contributing.

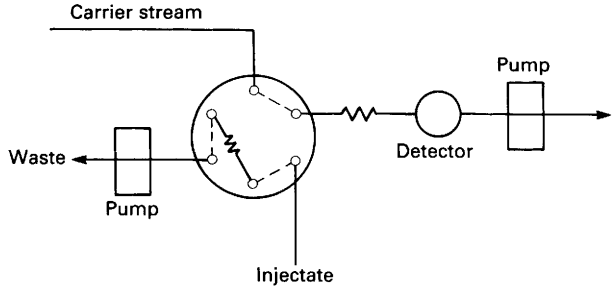

Fig. 1. Manifold and valve configuration used for time-based injections

The reaction studied uses three reagents, *viz.*, iodate, iodide and hydrogen ions. The concentration of iodate used was several orders of magnitude less than the concentrations of iodide and hydrogen ion and, therefore, its concentration would usually be limiting, *i.e.*, it would be expected to limit the amount of iodine formed at most points in the dispersing system. A variety of combinations of these reagents can be used to form iodine in a single-channel FI manifold. Each of the reagents can be in either the injectate or the carrier stream or in both. If all three reagents are in the same solution then the iodine is formed before injection, but this was not considered as a possible combination here. The most useful analytical system, *i.e.*, that used for the determination of sulphite with a small injection volume, is one in which acid is injected into a slightly alkaline carrier stream containing iodate and iodide, iodine being formed in the rFI manner. The signals obtained can be compared directly with the system in which an iodate - iodide solution is injected into an acidic eluent and in which iodine is formed in the nFI manner (for a small injection volume). These two systems were studied here using large injection volumes, as were all other possible reagent combinations.

Further restrictions on the number of combinations are as follows. Two solutions are used: these will have different compositions as all three reagents cannot be present together. Each solution can be used as the injectate or as the carrier stream so that each combination of reagents provides two experimental systems. Clearly, each reagent must be present in at least one solution and one of the solutions must contain two reagents. The second solution can contain one or two reagents. There is a total of six pairs of systems and these are listed and identified in Table 1.

Typical signals obtained with these systems using both slug and time-based injections are shown in Figs. 2 and 3, respectively. The heights of the two peaks for each system are compared in Tables 2 and 3. When iodate and iodide are present together in either the injectate or the carrier stream, the solution was made slightly alkaline to prevent premature

Table 1. Combinations of reagents by which iodine can be formed on-line in a single-channel manifold. Iodate is present in solution A in all combinations. In systems designated a, solution A is the carrier stream. In systems designated b, solution B is the carrier stream, *e.g.*, for system 4a, the carrier stream contains $IO_3^-H^+$ and the injectate I^-H^+. A particular reagent is present in both solutions (A and B) only in one combination

Combination number	Composition of solution A	Composition of solution B	Comments
1	$IO_3^-I^-$	H^+	
2	$IO_3^-H^+$	I^-	
3	IO_3^-	I^-H^+	
4	$IO_3^-H^+$	I^-H^+	H^+ in both solutions
5	$IO_3^-I^-$	I^-H^+	I^- in both solutions
6	$IO_3^-H^+$	$IO_3^-I^-$	IO_3^- in both solutions

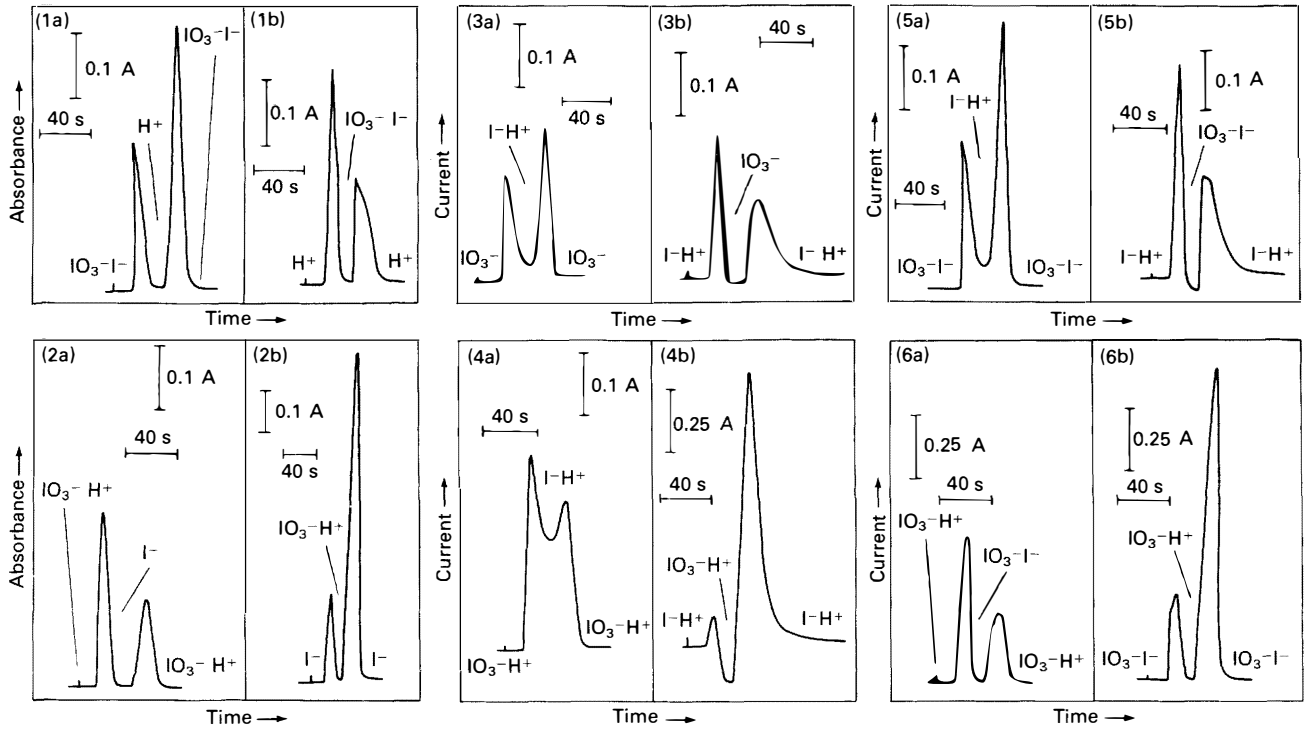

Fig. 2. Signals obtained with slug injections for different systems. The signals are numbered according to the information given in Table 1. Experimental conditions are given in the text. Flow-rate, 5 ml min^{-1}. Iodate, iodide and hydrochloric acid solution concentrations, 6.67×10^{-6} M, 0.23% and 0.1 M, respectively: non-acidic solutions were adjusted to pH 11.0 with sodium hydroxide solution

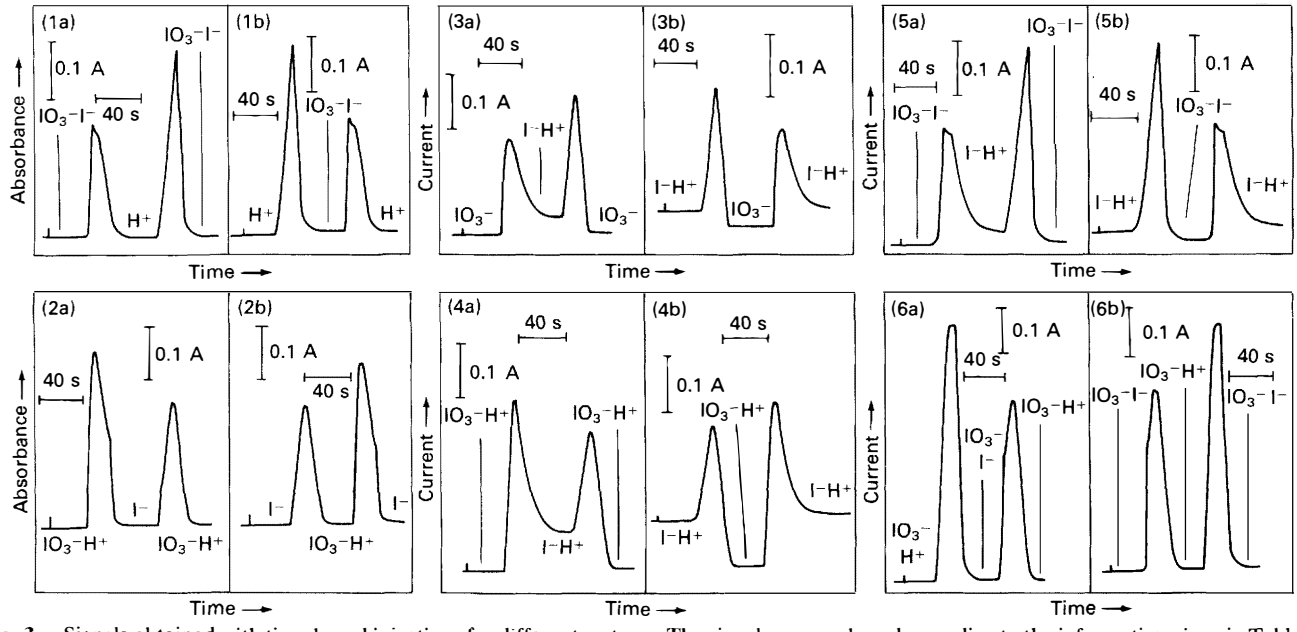

Fig. 3. Signals obtained with time-based injections for different systems. The signals are numbered according to the information given in Table 1. The experimental conditions are described in the text. Flow-rate, 2 ml min^{-1}; injection time, 1 min. Iodate, iodide and hydrochloric acid solution concentrations, 6.67×10^{-6} M, 0.23% and 0.1 M, respectively: non-acidic solutions were adjusted to pH 11.0 with sodium hydroxide solution

formation of iodine. The signals were obtained under the following experimental conditions: flow-rate, 2 and 5 ml min^{-1} (time-based and slug injections, respectively); injection time (time-based injection), 1 min; injection volume, 2.0 ml; iodate, iodide and hydrochloric acid concentrations, 6.67×10^{-6} M, 0.23% and 0.1 M, respectively; non-acidic solutions were adjusted to pH 11.0 with sodium hydroxide solution.

The most remarkable feature of the signals obtained concerns those for time-based injections. For the two complementary systems of each combination (where the same two solutions are used but in reversed roles) the two pairs of peaks obtained in each instance are identical except that they appear in reverse order, *i.e.*, the front peak of one signal is identical with the reverse peak of the other. In comparing some of the signals, allowance has to be made for the slow formation of iodine by air oxidation of iodide when the latter is present in acidic solution. Clearly, as might be expected, the shapes of the peaks obtained are determined by the solutions on either side of the individual boundaries. Hence identical peaks in complementary systems arise, for example, from solution A moving behind and into solution B; this produces the front peak of one system and the rear peak of its complementary

Table 2. Peak absorbances obtained for slug injections (< denotes the direction of the boundary shape)

System	Boundary	Peak absorbance	Boundary	Peak absorbance
1a	$IO_3^-I^- < H^+$	0.24	$H^+ < IO_3^-I^-$	0.43
1b		0.17		0.34
2a	$IO_3^-H^+ < I^-$	0.27	$I^- < IO_3^-H^+$	0.14
2b		0.81		0.23
3a	$IO_3^- < I^-H^+$	0.16*	$I^-H^+ < IO_3^-$	0.23*
3b		0.13*		0.23*
4a	$IO_3^-H^+ < I^-H^+$	0.30*	$I^-H^+ < IO_3^-H^+$	0.23*
4b		1.21*		0.26*
5a	$IO_3^-I^- < I^-H^+$	0.23*	$I^-H^+ < IO_3^-I^-$	0.41*
5b		0.18*		0.34*
6a	$IO_3^-H^+ < IO_3^-I^-$	0.58	$IO_3^-I^- < IO_3^-H^+$	0.29
6b		1.23		0.36

* No allowance was made in measuring these peak heights for the presence of iodine formed by air oxidation of iodide in acidic solution. The peak absorbance was measured on the side of the peak where the larger change of absorbance occurred.

Table 3. Peak absorbances obtained for time-based injections

System	Boundary	Peak absorbance	Boundary	Peak absorbance
1a	$IO_3^-I^- < H^+$	0.20	$H^+ < IO_3^-I^-$	0.34
1b		0.20		0.34
2a	$IO_3^-H^+ < I^-$	0.32	$I^- < IO_3^-H^+$	0.23
2b		0.30		0.22
3a	$IO_3^- < I^-H^+$	0.17*	$I^-H^+ < IO_3^-$	0.25*
3b		0.17*		0.25*
4a	$IO_3^-H^+ < I^-H^+$	0.31*	$I^-H^+ < IO_3^-H^+$	0.25*
4b		0.30*		0.26*
5a	$IO_3^-I^- < I^-H^+$	0.22*	$I^-H^+ < IO_3^-I^-$	0.37*
5b		0.21*		0.36*
6a	$IO_3^-H^+ < IO_3^-I^-$	0.54	$IO_3^-I^- < IO_3^-H^+$	0.37
6b		0.51		0.37

* No allowance was made in measuring these peak heights for the presence of iodine formed by air oxidation of iodide in acidic solution. The peak absorbance was measured on the side of the peak where the larger change of absorbance occurred.

system. Similarities of shape can also be seen in Fig. 2 for slug injections, but the difference in peak heights for the same boundary reflects the difference in dispersion depending on whether the boundary is at the front or rear of the injected bolus.

On further examination of the time-based signals in Fig. 3 it becomes clear that the signals obtained for combinations 1 ($IO_3^-I^- < H^+$) and 5 ($IO_3^-I^- < I^-H^+$) (< denotes the direction of the boundary shape) are also identical. Clearly, provided that iodide is present with iodate in one solution, the presence of iodide with H^+ in the other solutions has no effect on the signals obtained. The peaks obtained for combination 3 ($IO_3^- < I^-H^+$) are different from those of combinations 1 and 5; clearly, moving I^- from the solution with IO_3^- to the solution with H^+ does affect the signal to some extent.

The peak shapes have a variety of characteristics in the various combinations. In some instances the peak starts and/or finishes abruptly from the base, or the base may be more rounded, or sometimes an intermediate situation is observed. A rectilinear rise and/or fall of the signal may be observed. For acid moving behind and into iodate - iodide, the peak rises vertically from an abrupt start. Some peaks are sharp, others are more or less rounded and some exhibit shoulders. The peaks for combination 6 in which iodate is present in both solutions are anomalously high, particularly for slug injections. Further, these peaks appear to reach a steady state and are almost flat-topped. Experiments were carried out to determine the true steady-state signal when iodine was formed fully off-line at an equivalent iodate concentration of 6.67×10^{-6} M and this solution was caused to flow through the manifold and was monitored. Obtaining this steady-state absorbance was not as straightforward as might have been expected owing to the air oxidation of iodide in acidic solutions. By extrapolating back to the time of mixing, a steady-state absorbance of 0.42 was obtained. The correction was relatively small and does not account for the much higher absorbances of the combination 6 peaks. Certainly the flat-topped signals might be expected for this combination as the (limiting) iodate concentration is initially the same throughout the carrier stream and the injected bolus. The experiments have been repeated, and at the moment we are at a loss to explain this apparent concentrating by diffusion of iodine and the iodine-forming species iodate during the dispersion.

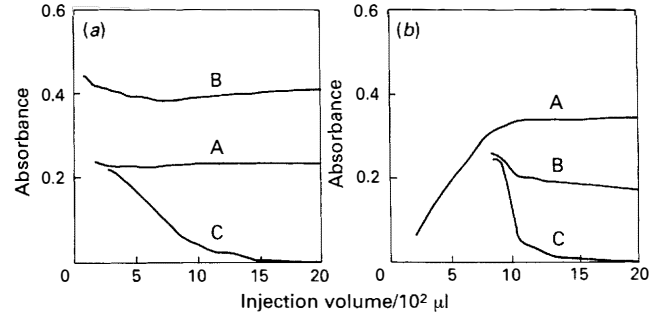

Fig. 4. Effect of injection volume on the height and integrity of the front and rear peaks for (*a*) $IO_3^-I^- < H^+ < IO_3^-I^-$ (system 1a) and (*b*) $H^+ < IO_3^-I^- < H^+$ (system 1b). Height (*i.e.*, absorbance) of A, front peak; B, rear peak; and C, valley between the peaks. Slug injection: flow-rate, 5 ml min^{-1}; $IO_3^-I^-$ solution, 6.67×10^{-6} M in KIO_3, 1.4×10^{-2} M in KI and 2×10^{-3} M in NaOH; H^+ solution, 0.1 M HCl

Effect of Reducing the Injection Volume on Peak Shapes

The studies described above of on-line formation of iodine with various combinations of reagents and with large-volume (2 ml) injections were carried out in order to observe the dispersion at the two boundaries of the bolus without interference from dispersion at the other boundary. Of particular interest is the system in which acid is injected into a carrier stream containing iodate and iodide. In the routine use of FI, however, small volumes (10–100 µl) are usually injected to obtain medium dispersion throughout the bolus, to obtain a single peak as the signal and to increase the throughput of samples. Previously sulphite has been determined with amperometric detection by injecting first acid and then an acidified solution of the sulphite sample into the iodate - iodide carrier stream.[5] The decrease in the size of the iodine peak was proportional to the sulphite concentration in the sample solution.

The shapes of the signals obtained in this earlier work[5] seemed to indicate that the peak obtained for the formation of iodine is determined mainly by the dispersion at the rear extremity of the bolus. To confirm this assumption, the effect of varying the slug injection volume from 2 ml to 100 µl was studied for this system and for its complementary system in which iodate - iodide is injected into an acid carrier stream.

In Fig. 4 (*a*) and (*b*) absorbance is plotted against injection volume for the injection of acid into iodate - iodide and of iodate - iodide into acid, respectively. Curve A in both instances gives the height of the front peak, curve B the height of the rear peak and curve C the height of the minimum (the valley) between them. Comparison of the curves in Fig. 4 (*a*) and (*b*) for an injection volume of 2 ml indicates that the back peak is the larger in Fig. 4(*a*) and the front peak in Fig. 4(*b*), as reported above (systems 1a and 1b, Fig. 2). As at this injection volume the peaks are completely separate the valley between them corresponds to zero absorbance. In both systems when

the injection volume is reduced very little change occurs in the heights of peaks A and B as they begin to merge, but as the peaks get closer together dispersion reaches the centre of the bolus, iodine is formed there and the height of the valley increases until eventually curves A and C [Fig. 4(*a*)] and B and C [Fig. 4(*b*)] merge as the smaller peak in each instance becomes a shoulder on the major peak and then becomes unobservable.

Note that the major peak in both instances is formed by dispersion of the same boundary, *viz.*, iodate - iodide moving behind and into acid. Further, note that at very small injection volumes the peak height (*i.e.*, the peak height of the remaining peak) for the injection of acid into iodate - iodide remains constant (or increases slightly), whereas that for the injection of iodate - iodide into acid decreases rapidly. At large injection volumes the terms nFI and rFI have no real meaning as dispersion is occurring at two independent boundaries and iodate remains in plentiful supply in both systems. For situations at lower injection volumes where a single peak is obtained, however, the terms do become meaningful. Hence with small injection volumes and extensive dispersion, there is still a plentiful supply of iodate in the rFI system but a decreasing supply in the nFI system. The signal at these low injection volumes is dominated by dispersion at one of the boundaries and this boundary is the same for the two complementary systems, that in which iodate - iodide is moving behind and into acid.

The increased difficulty of obtaining a single peak when changing from nFI to rFI has been noted previously.[2,5] An indication of the reason for this can be obtained from Fig. 4. For nFI a single peak is obtained for injection volumes of less than *ca.* 800 μl, whereas a single peak in the rFI system is obtained only at injection volumes of less than *ca.* 200 μl for the conditions used in these experiments.

The information obtained in this work has been used to optimise a method for the determination of sulphite using spectrophotometric detection in which iodine is formed in the rFI manner. This will be reported separately. Further studies of the shapes of FI signals are being carried out using simpler systems than the present ones. The iodine systems studied here require three reagents and are complicated further by the slow oxidation of iodide to iodine in acidic solutions by dissolved molecular oxygen.

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