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Shapes of Flow Injection Signals: Effect of Refractive Index on Spectrophotometric Signals Obtained for On-line Formation of Bromine From Bromate, Bromide and Hydrogen Ion in a Single-channel Manifold Using Large-volume Time-based Injections[*]

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The shapes of the spectrophotometric signals obtained with a single-channel manifold for large-volume (4 ml) time-based injections for the six possible combinations of the reagents bromate, bromide and nitric acid in the injectate and carrier stream, by which bromine can be formed on-line, have been determined. The injectate and carrier stream were 5.25×10^{-4} M in bromate, 0.030 M in bromide and 1 M in nitric acid when these reagents were present. The signals consisted of two separate peaks caused by formation of bromine at the front and rear boundaries of the injected bolus. When both injectate and carrier stream were 1 M in nitric acid (*i.e.*, for the reagent combination $H^+BrO_3^-$ - H^+Br^-) the two peaks were of equal height, and the signal was virtually the same whichever solution was used as the injectate. In reagent combinations where only one solution contained nitric acid the peaks were different in size, the smaller peak being that produced by the boundary in which the acidic solution was flowing behind the other solution. This difference in size between the front and rear peaks was shown to be caused by refractive index effects. When the refractive indices of the two solutions were matched either by increasing the potassium bromide concentration or by making the non-acidic solution 7% in sodium nitrate, the peaks became equal in size. When the potassium bromide concentration was increased there was an appreciable increase in peak size (about 4-fold): the changes in the amount of bromine formed must be due to kinetic or equilibrium effects. This increase in size did not occur when sodium nitrate was used to balance the refractive indices.

Keywords: *Flow injection; spectrophotometric detection; on-line bromine formation; refractive index effect; large-volume and time-based injections*

Interest in flow injection signal shapes in this series of studies arose from the application of reverse flow injection (rFI) amperometric methods in single-channel manifolds. Reverse flow injection was used in two ways: either (*i*), reagent was injected into a sample stream[1]; or (*ii*), a monitorand was formed in the bolus by dispersion of a concentration limiting reagent contained in the carrier stream. This monitorand then reacted with a determinand which had been injected with an excess of a second reagent used to form the monitorand.[2–4] Examples of these two ways of using rFI are the determination of phosphate by injecting an acidified molybdate reagent into a phosphate sample stream,[1] and the iodimetric determination of sulphite in which iodine is formed on-line from iodate (and an excess of iodide) in the carrier stream, and an excess of acid, present with sulphite, in the injectate.[4] In these methods conventional injection volumes (*ca.* 100 µl) were used.

It eventually became clear that rFI signals were different in shape from the more conventional or normal flow injection (nFI) signals.[4,5] The schematic diagram (Fig. 1) illustrates simply the formation of nFI and rFI signals. In nFI the product is formed initially at the extremities of the bolus, but soon sufficient reagent has reached the centre of the bolus for all the sample to be converted to product: further dispersion simply dilutes this product. The conventionally shaped flow injection signal is obtained. The main difference between the nFI and rFI situations is that in rFI the sample is present essentially in infinite supply in the carrier stream. The equivalent concentration of sample throughout the reagent bolus increases from zero to a value approaching that in the carrier stream. Clearly, rFI signals would be expected to be broader than nFI signals and more prone to double-peak formation (especially when a determinand is injected into a monitorand formed in the rFI manner). The formation of double peaks was observed in the amperometric monitoring of iodine formed in the rFI manner, and this became more apparent when sulphite was injected with the acid (see Fig. 3 in reference 4).

Recently, the on-line formation of iodine was monitored spectrophotometrically in order to gain greater insight into the shapes of these signals.[6] Large-volume (2 ml) injections were used to isolate the dispersions at the front and rear boundaries of the injected bolus. Time-based injections, where both boundaries travel the same distance to the detector, were used to eliminate differences in dispersion caused by the rear boundary travelling further than the front boundary, which

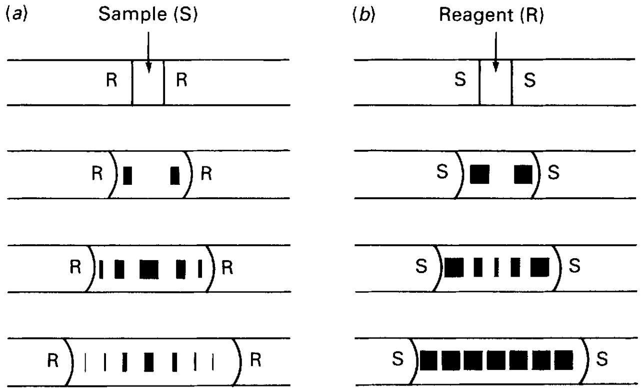

Fig. 1. Schematic diagram showing the formation of (*a*) nFI and (*b*) rFI signals, as dispersion increases with the distance travelled by the bolus in the transmission tubing. The size of each shaded area represents the extent of formation (*i.e.*, the concentration) of the reaction product which is monitored at the detector

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[*] Presented at SAC 89, the 8th International Conference on Analytical Chemistry, Cambridge, UK, 30 July–5 August, 1989.

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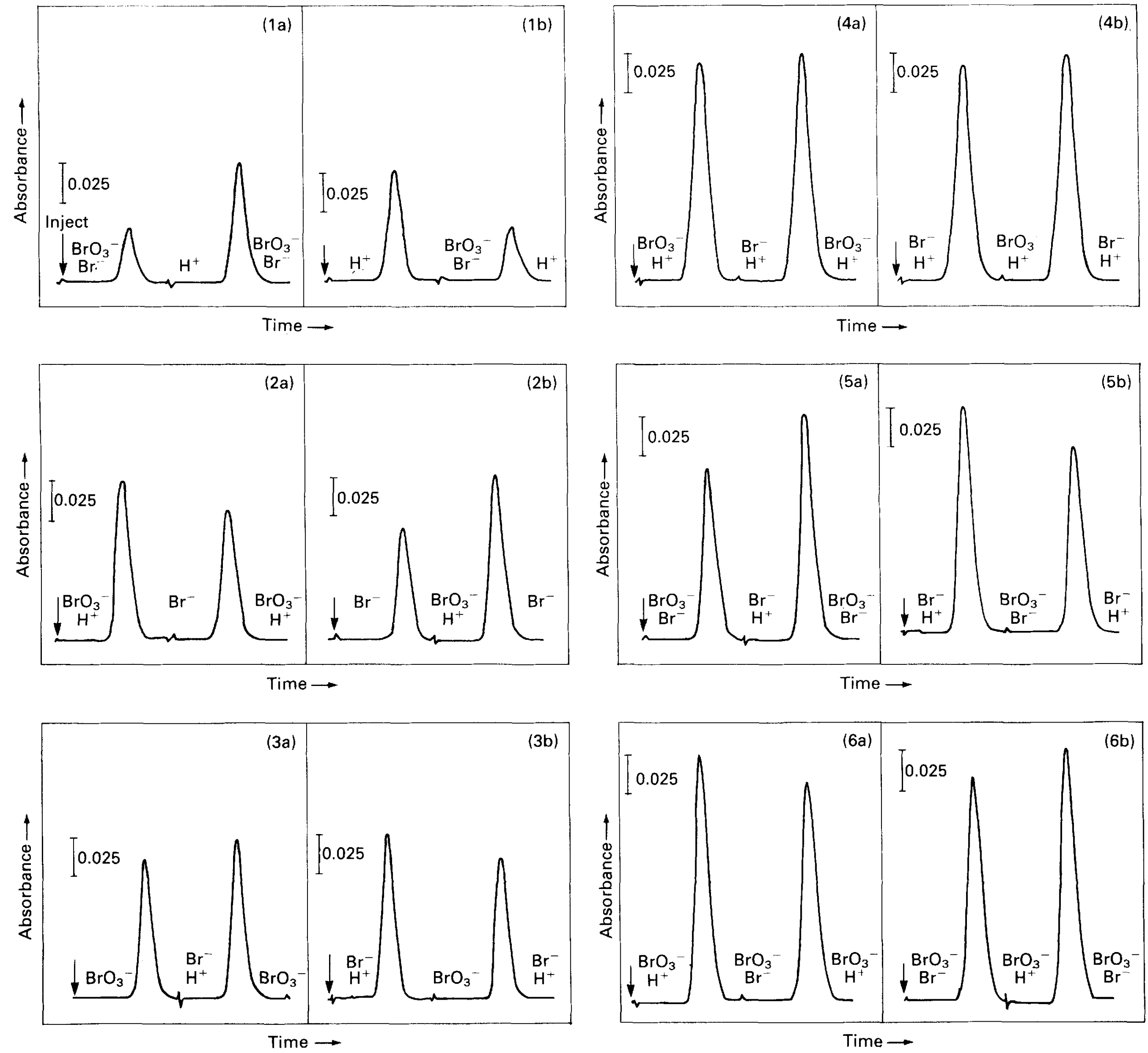

Fig. 2. Signals obtained with time-based injections for different combinations of reagents. The signals are numbered according to the information given in Table 1. The experimental conditions are described in the text. Flow-rate, 2 ml min^{-1}, [bromate], 5.25×10^{-4} M; [bromide], 0.030 M; and [nitric acid], 1 M. Non-acidic solutions were adjusted to pH 11.0 with sodium hydroxide solution. (The disturbance of the signal between the peaks is caused by the injection valve switching back to the carrier stream)

occurs in slug injection. Three reagents are used in the on-line formation of iodine, *viz.*, iodate, iodide and acid. These are present in two solutions. One solution must contain two of the reagents, but the other solution may contain one or two reagents, *i.e.*, one reagent can be present in both solutions. Thus, there are six possible reagent combinations, each of which is represented by two practical systems because each solution can serve as injectate or carrier stream. At large injection volumes each signal consisted of two peaks caused by iodine formation at the front and rear boundaries independently. The signals for four reagent combinations, including IO_3^--I^- - H^+, showed clearly that the size and shape of each particular peak (half of the signal) was determined simply by the composition of the solutions at the boundary and their positions relative to each other in the flow stream; for these four combinations of reagents the two peaks of each signal were clearly of different heights. Thus, for the reagent combination IO_3^--I^- - H^+ the larger peak was the one produced by the boundary in which the acidified solution was in the front. Unfortunately, for the two combinations of reagents which involved iodide and acid being present in the same solution interpretation of the signals was difficult because of the formation of iodine by oxidation by air.

In the present work the on-line formation of bromine by reaction of bromate, bromide and acid was monitored spectrophotometrically. It was felt that the results of this study could be interpreted more readily than those of the iodine system because bromine is not formed by air oxidation of bromide in acidified solutions.

Experimental

A single-channel manifold incorporating a six-port rotary valve was used to carry out time-based injections under computer control as described previously.[6] The transmission tubing was made of PTFE (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. Bromine was monitored at 393 nm. To study the refractive index effects measurements were also made at

550 nm where absorption by bromine was negligible. Refractive index measurements were made with an Abbe refractometer.

Results and Discussion

Nitric acid was used as the source of hydrogen ion: the use of hydrochloric acid was avoided because chloride is oxidised to chlorine by bromate, and was shown to distort the flow injection signals. The combinations of reagents by which bromine can be formed on-line in a single-channel manifold are listed in Table 1: these are numbered in a manner identical with the iodine system which was studied previously.[6] Typical signals obtained with these systems using time-based injections are shown in Fig. 2. The signals were obtained under the following experimental conditions: flow-rate, 2 ml min^{-1}; injection volume, 4 ml; bromate, bromide and nitric acid concentrations, 5.25 × 10^{-4}, 0.030 and 1 M, respectively; non-acidic solutions were adjusted to pH 11.0 with a sodium hydroxide solution. Note that the bromate concentration (5.25 × 10^{-4} M) used was two orders of magnitude higher than that of the iodate (6.67 × 10^{-6} M) used in the previous study,[6] because of the lower molar absorptivity of bromine.

The signals shown in Fig. 2 can be compared with those obtained previously for the iodine system.[6] In the present system the base lines obtained for all combinations of reagents remained at the same zero absorbance level for injectate and carrier stream because there was no problem with extraneous formation of bromine by air oxidation. Thus, with bromine the signals from all the combinations are available for more immediate interpretation than those for the iodine system. When the role of the two solutions is reversed the position of the peaks is reversed for all combinations. For all combinations here it can be seen that the height and shape of each peak (half signal) is determined by the composition of the two solutions at the boundary producing the signal and their relative positions in the flow stream. This was observed unambiguously for only four of the combinations in the iodine system, the situation in the other two combinations being obscured by air oxidation problems. The main feature that can be seen in the bromine system, but not in the iodine system, is that for systems 4a and 4b the two peaks of each signal are of approximately equal height; in this reagent combination acid is present in both solutions. At this stage it was considered that the faster rate of diffusion of hydrogen ion might explain the unequal peak heights observed with combinations other than 4, but this was eventually proved not to be the case.

At this stage in the experimental work the effect of including sulphite with the nitric acid in system 1a on the size and shape of the two peaks obtained in the 4-ml injection was studied. This system is the same as that reported recently for the spectrophotometric determination of sulphite using system 1a,[7] except that a 4-ml time-based injection is made here instead of a 15-μl slug injection. The effect of injecting nitric acid solutions containing an increasing amount of sulphite is shown in Fig. 3(*a*)–(*f*). The highest concentration of sulphite used is sufficient to reduce any bromine formed, but a large signal consisting of a negative peak and a positive peak remains. Clearly this effect is due to refractive index differences between the two solutions used as carrier stream and injectate. This we should have anticipated as Betteridge *et al.*[8] have demonstrated pronounced refractive index effects in single-channel manifolds using conventional FI injection volumes. The refractive index of an electrolyte solution increases with concentration, and the refractive index of a 1 M

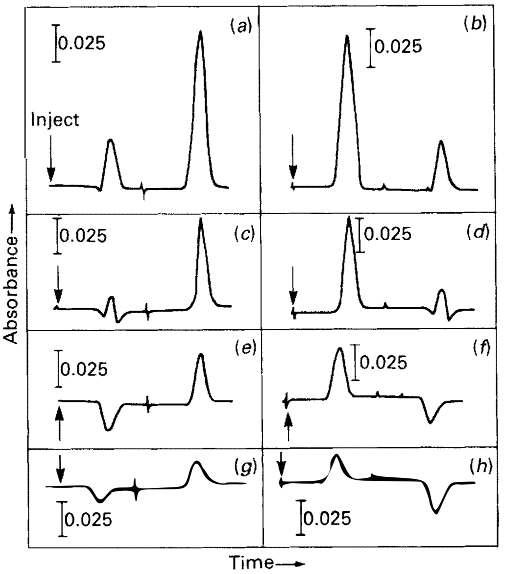

Fig. 3. (*a*)–(*f*) Signals obtained at 393 nm when increasing concentrations of sulphite were added to the nitric acid in reagent combination 1. [Sulphite]: (*a*) and (*b*), 2.87 × 10^{-5} M; (*c*) and (*d*), 2.87 × 10^{-4} M; and (*e*) and (*f*), 2.87 × 10^{-3} M. (*g*) Signal obtained when 1 M nitric acid solution was injected into water and (*h*) *vice versa*

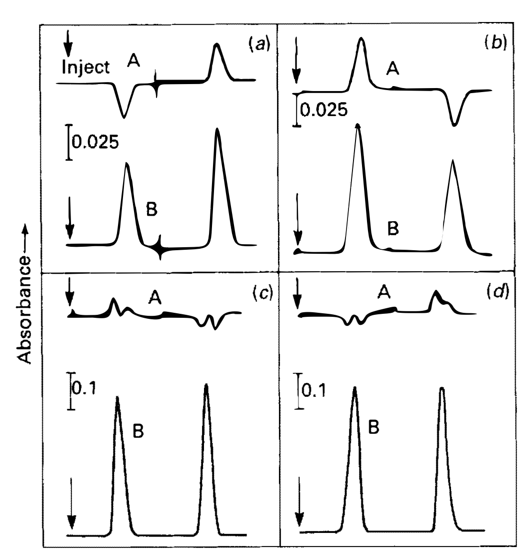

Fig. 4. Effect of balancing the refractive indices of injectate and carrier stream, by increasing the concentration of potassium bromide, on the signals obtained at A, 550 and B, 393 nm for reagent combination 1. [Potassium bromide]: (*a*) and (*b*) 0.030 M; and (*c*) and (*d*) 3.00 M. (*a*) and (*c*) Carrier, $BrO_3^-Br^-$; injectate, H^+; and (*b*) and (*d*) carrier, H^+; injectate, $BrO_3^-Br^-$

Table 1. Combinations of reagents by which bromine can be formed on-line in a single-channel manifold. Bromate 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 $BrO_3^-H^+$ and the injectate Br^-H^+. A particular reagent is present in both solutions (A and B) in one combination

Combination number	Composition of solution A	Composition of solution B	Comments
1	$BrO_3^-Br^-$	H^+	
2	$BrO_3^-H^+$	Br^-	
3	BrO_3^-	Br^-H^+	
4	$BrO_3^-H^+$	Br^-H^+	H^+ in both solutions
5	$BrO_3^-Br^-$	Br^-H^+	Br^- in both solutions
6	$BrO_3^-H^+$	$BrO_3^-Br^-$	BrO_3^- in both solutions

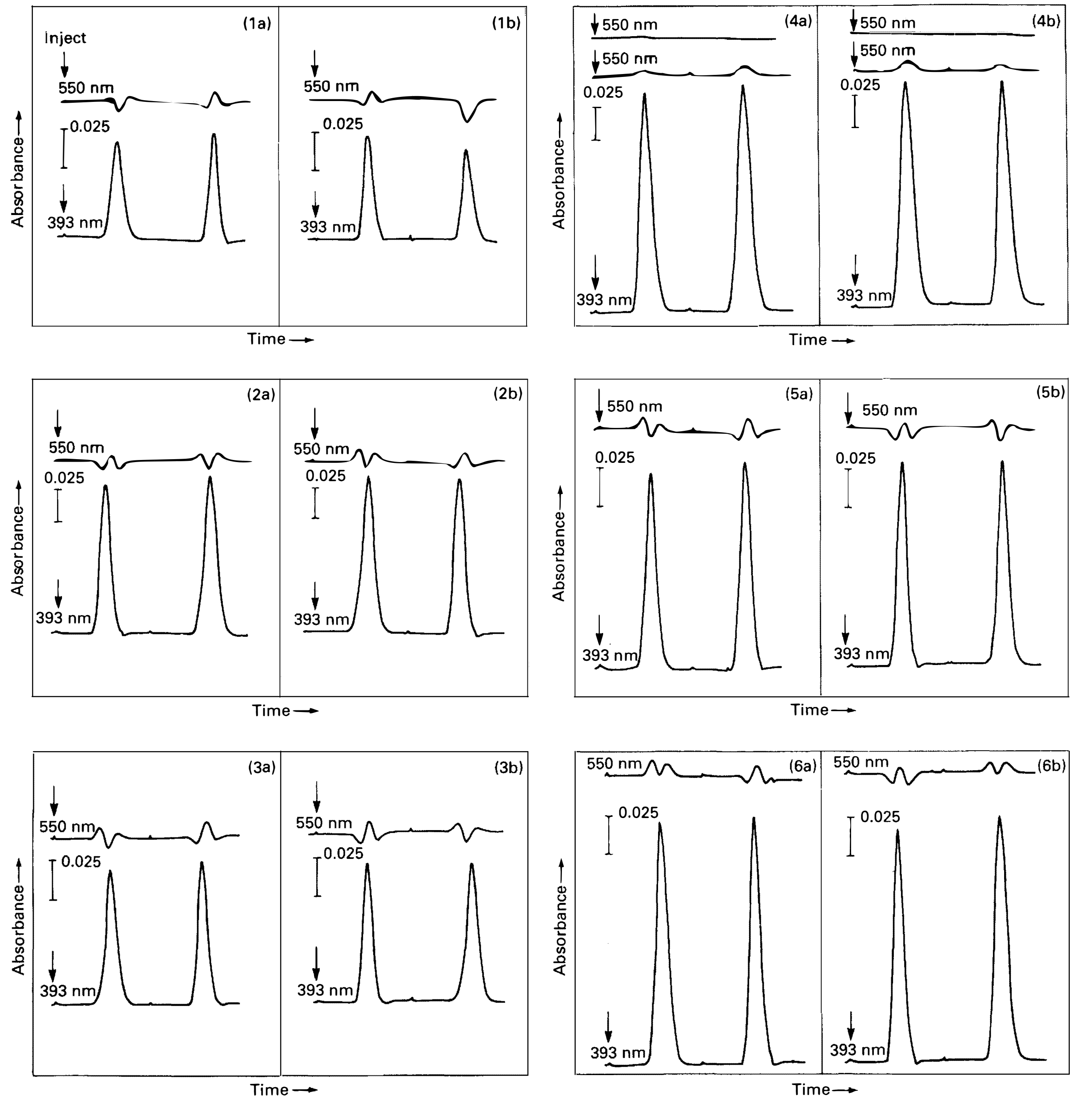

Fig. 5. Effect of balancing refractive indices in all combinations by making non-acidic solutions (and both solutions for system 4) 7% m/v in sodium nitrate. For combination 4 the signal at 550 nm is also recorded in the absence of bromate to illustrate the residual bromine signal. The signals are numbered according to the information given in Table 1

nitric acid solution is appreciably higher (1.3405) than those of 0.03 M potassium bromide (1.3330) or 5 × 10^{-4} M potassium bromate solution. As can be seen in Fig. 3(*g*) and (*h*), similar signals were obtained when 1 M nitric acid solution was injected into a water carrier stream and *vice versa*. A study of the effect of sulphite addition on the two-peak signals was postponed pending further studies of the refractive index effect and is not reported further here.

The effect of balancing the refractive indices of the two solutions was observed. The effect was first checked for reagent combination 1 by increasing the concentration of potassium bromide. When the potassium bromide concentration in the carrier stream had been increased 20-fold (refractive index of carrier stream 1.3405) the heights of the two peaks measured at 393 nm became equal (see Fig. 4). In order to study the refractive index signal without interference from the bromine signal measurements were also made at 550 nm, at which wavelength the bromine signal was negligible. The size of the signal at 550 nm for the carrier stream with the high potassium bromide concentration was much reduced, but was not eliminated. The addition of more bromide not only caused the peaks at 393 nm to become equal in height but the peaks obtained were considerably larger than before, indicating that more bromine is formed under these new solution conditions. This must be caused by kinetic or equilibrium effects in the formation of bromine.

The effect of making the non-acidic solutions (or both solutions in the case of combination 4) 7% m/v in sodium nitrate is shown in Fig. 5. This addition results in much closer matching of peak heights. Note that at 550 nm for combination

4 the signal is purely positive, which may indicate that there is a residual bromine signal at this wavelength; one would expect the refractive index signal in this combination to be eliminated completely. This was confirmed by monitoring the signal at 550 nm after omitting bromate from the solutions and explains the shapes of the signals for other combinations at 550 nm. Note also that on the addition of sodium nitrate there is no large increase in peak height as was the case when extra potassium bromide was added.

Clearly, when using flow injection with spectrophotometric detection in single-channel manifolds one should be aware of the effects of changes in refractive index on the signals obtained. However, even if a refractive index component is present in the observed signals, calibration graphs will still be valid provided that the standard and sample solutions are similar in composition. Alternatively, the effect of refractive index can be eliminated by matching the refractive indices of the injectate and carrier stream as illustrated above. The present work on large-volume injections is being extended to observe the effects of refractive index and refractive index matching on the signals obtained with small-volume injections. Further work is in progress on the shapes of flow injection signals obtained in single-channel manifolds using both visible spectrophotometric and amperometric detection.

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