

## THE EFFECT OF SUBSTANCE DIFFUSIBILITY ON THE SENSITIVITY AND PEAK SHAPE OF DIFFERENT INJECTION MODES IN A SINGLE-CHANNEL FLOW INJECTION MANIFOLD

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### ABSTRACT

In this paper, the differences of double-peak shapes between two injection modes in a single-channel flow injection manifold were studied and explained with fluid dispersion theory. It was discovered that the substance diffusion coefficient ( $D_m$ ) has significant influence on these differences. To a certain chemical reaction system, the sensitivity obtained by injecting a larger  $D_m$  substance into a smaller  $D_m$  substance is lower than that obtained by injecting inversely. Furthermore, when the injection volume is large enough to form double peaks, a double peak with higher rear peak will be obtained by injecting a larger  $D_m$  substance into a smaller  $D_m$  substance while a double peak with higher front peak will be obtained by injecting inversely.

### INTRODUCTION

In flow injection analysis (FIA), there are two injection modes which have been used for a single-channel manifold: one is normal flow injection

analysis (nFIA) in which a sample is quantitatively injected into a reagent as carrier stream; the other one is the reversed flow injection analysis (rFIA) in which a reagent is quantitatively injected into a sample as carrier stream. rFIA was firstly reported by Johnson & Petty<sup>1</sup> in 1982. They studied the dispersion of sample and reagent by a "tanks-in-series" model and proved by experiment that rFIA had higher sensibility than nFIA though it was just reversing the injection phase. Tyson<sup>2</sup>, the Valcarcel group<sup>3</sup> and Chen<sup>4</sup> all basically agreed in their later researches that rFIA had a higher sensibility than nFIA. However, the experiments of Rois<sup>5</sup> indicated that rFIA didn't always have a higher sensibility than nFIA.

For the purpose of further investigating the relationship of peak shapes between nFIA and rFIA, Fogg and co-workers<sup>6</sup>, using a large injection volume which allows double peaks to be formed, found that the flow direction of the reagent had effect on the peak heights and peak shapes. Unfortunately, he didn't point out the reasons for the sensibility and peak

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shapes' differences. According to the research work in this paper, it shows that the diffusion coefficients of reagent and sample are critical for these differences of sensitivity and double-peak shapes. This discovery thus consummated the peak theory of FIA.

## Theory

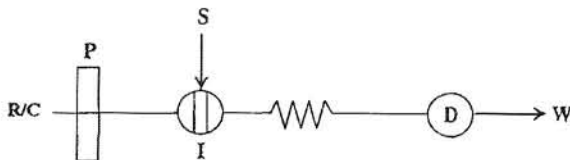


Figure 1. Manifold of the single-channel flow injection system

P: peristaltic pump    I: injection valve    D: detector  
S: sample            R/C: reagent/carrier    W: waste

These definitions are valid for any single-channel manifold, of course, and can be extended to any point on the reagent or sample profile (Fig. 2):

$$D_g^S = C_0^S / C_g^S$$

$$D_g^R = C_0^R / C_g^R$$

where  $C_g$  is the concentration at any point on the dispersed profile.

According to the experiment of Tyson, if  $D_g^S$  was determined by injecting a color analyte into  $H_2O$  and  $D_g^R$  was determined by injecting  $H_2O$  into the same color analyte,  $1/D_g^S + 1/D_g^R = 1$ . This was proved by theoretical deduction. Fang et al.<sup>7</sup> also confirmed this in their experiments.

In a single-channel flow injection analysis, the sample dispersion during the flow towards the detector is composed of two parts: one is the convection dispersion which is caused

## 1. Effect of $D_m$ on the sample/reagent dispersion

In a single channel flow injection manifold (Fig. 1), the dispersion coefficients of sample and reagent is defined as  $D^S = C_0^S / C_P^S$  and  $D^R = C_0^R / C_P^R$ , respectively ( $C_0$ : steady state concentration,  $C_P$ : peak concentration).

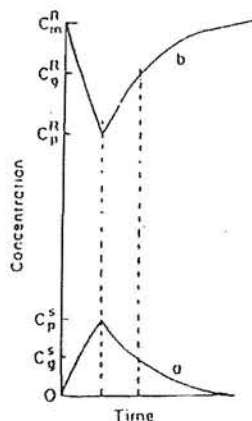


Figure 2. Concentration profiles of dispersed sample (a) and reagent (b) with no chemical reactions.

by the flow of the carrier and is directly proportional to the value of the flow rate; the other one is the diffusion dispersion which is caused by the diffusion of the analyte and is directly

proportional to the diffusion coefficient of the analyte. For a certain manifold, the convection dispersion part remains constant. Therefore, higher dispersion can be obtained for larger analyte diffusion coefficient. Then,  $1/D_g^S + 1/D_g^R < 1$  can be obtained when larger Dm sample is injected into smaller Dm reagent carrier, i.e., the sample and reagent are relatively diluted;  $1/D_g^S + 1/D_g^R > 1$  can be obtained when smaller Dm sample is injected into larger Dm reagent carrier, i.e., the sample and reagent are relatively concentrated. In general flow injection analysis, the Dm of sample is usually

larger than that of reagent. Therefore, the sample and reagent are usually relatively concentrated in rFIA. This is why rFIA usually has a higher sensitivity than nFIA.

## 2. Effect of the diffusion coefficient on double peak shapes under two injection modes - nFIA & rFIA

The substance injected in the form of plug flow into the fluid in a round tube and doing an isothermal and incompressible flow has a dispersion model that can be expressed by equation (1)<sup>8</sup>

$$\tau \frac{\partial C}{\partial t} = Ez \left( \frac{\partial^2 C}{\partial l^2} \right) + Er \left( \frac{\partial^2 C}{\partial r^2} + r^{-1} \cdot \tau \frac{\partial C}{\partial r} \right) \cdot u \cdot \frac{\partial C}{\partial l} \quad (1)$$

where C is the concentration of injected analyte; Ez and Er are the axial and radial dispersion coefficient, respectively; l and r represent the lateral direction and the radial direction; u is the average flow rate. As Er is much less than Ez and is negligible, the dispersion model can be simplified as:

$$\frac{\partial C}{\partial t} = Ez \left( \frac{\partial^2 C}{\partial l^2} \right) - u \cdot \frac{\partial C}{\partial l} \quad (2)$$

Let  $C^* = C/C_0$ ,  $\theta = t/\tau$  and  $z = l/L$ , where L is the length of the tube and  $\tau$  is the average residence time,  $\tau = L/u$ . Equation (2) then can be rewritten in a dimensionless form as equation (3) as follows:

$$\frac{\partial C^*}{\partial \theta} = (Ez/ul) \cdot \frac{\partial^2 C^*}{\partial z^2} - \frac{\partial C^*}{\partial z}$$

In FIA, the stream of carrier is in transitional motion and the corresponding condition of boundaries is open mode. Using the numerical methods solution, equation (3) can be

described by series of E curve as shown in Fig. 3.

As can be seen in Fig. 3, the peak maximum of the E curve is moving forwards with increasing Ez/ul.

In FIA, the residence time (Tr) is defined as the time span between the sample injection and the peak maximum that yields the analytical readout as peak height. For a certain FIA system, u, L,  $\tau$  is constant. Obviously Tr will increase with the increase of the value of Ez.

For laminar flow in a round tube,  $Ez/ud = 1/(Re \cdot Sc) + Re \cdot Sc/192^9$  (4) where Re is Reynolds number,  $Re = du\rho/\mu$ ,  $Sc = \mu/(\rho \cdot Dm)$  in which d is tube inner diameter,  $\rho$  is the fluid density,  $\mu$  is the fluid viscosity.

If  $Re \cdot Sc < 3$ , then  $Ez = Dm$ ,

If  $3 < Re \cdot Sc < 50$ , then

$$Ez = (ud)^2 / (192Dm)$$

If  $Re \cdot Sc > 50$ , then

$$E_z = D_m + (ud)^2 / (192D_m)$$

In FIA systems, the flow is a laminar flow. A typical FIA system, having an inside diameter of 0.05cm,

and  $u$  between 0.5 and 3.0ml/min, has a  $Re$  value of  $20-130^{10}$ . For all liquids,  $Sc$  is in

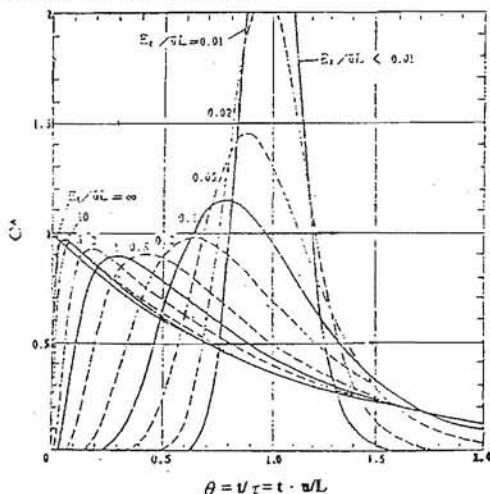


Figure 3 E curves in closed boundary condition

the range of about  $250-2500^{11}$ . Thus, in a FIA system,  $Re \cdot Sc > 50$ , then,

$$E_z = (ud)^2 / (192D_m) \quad (5)$$

It can be seen from equation (5) that  $E_z$  is inversely proportional to  $D_m$ , i.e., longer residence time ( $T_r$ ) will be obtained for the sample that has larger diffusion coefficient. For this reason,

injecting larger  $D_m$  sample into smaller  $D_m$  reagent carrier will form a double-peak with a higher rear peak as shown in Fig. 4(a); injecting smaller  $D_m$  sample into larger  $D_m$  reagent carrier will form a double-peak with a higher front peak as shown in Fig. 4(b).

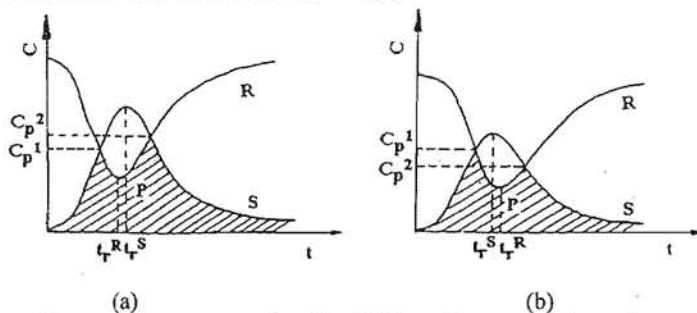


Figure 4 The concentration distributions of reagent and sample  
 (a) the  $D_m$  of sample is larger than that of the reagent  
 (b) the  $D_m$  of the sample is smaller than that of the reagent

## Experimental

### Reagent

$0.67 \times 10^{-3}$  M  $\text{KIO}_3$  stock solution: Dissolve 1.400g  $\text{KIO}_3$  in 500ml  $\text{H}_2\text{O}$ . Dilute it to  $6.67 \times 10^{-6}$   $\text{KIO}_3$  in 1.0M HCl before use.

3.0% KI stock solution: dissolve 3.0g KI in 100ml  $\text{H}_2\text{O}$ , the pH was adjusted to 11.0. Dilute it to 0.3% KI in 1.0M HCl before use.

Other colored inorganic chemicals such as  $\text{CuSO}_4$ ,  $\text{K}_3\text{Fe}(\text{CN})_6$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$  were also used as samples.

All reagents were of analytical reagent grade and were obtained from Peking Chemical Works, Peking, China. All solutions were prepared with distilled water.

### Apparatus

An FIA-91 Flow Injection Analyzer (made in Shanghai No.3 Analytical Instrument Factory) was used. This is a integrated instrument which consists of two 4-channel peristaltic pumps, a 16-port valve, a grating spectrophotometric detector, a Laser PP40 X-Y Printer plotter and a microcomputer system. Program control and data processing are conducted automatically by the microcomputer system.

### Procedure

The single-channel flow injection manifold used is shown in Fig. 1. The effect of diffusion coefficient on the dispersion of sample/reagent is

observed by injecting samples/reagents that have various diffusion coefficients.

## Results and Discussion

### Effect of diffusion coefficient on the dispersion of sample/reagent

In order to investigate the effect of  $D_m$  of a analyte on the dispersion, an FIA system with no chemical reaction were used and colored substance solutions were directly used as analyte. The FIA system was fixed as: sample injection volume  $V_{inj}=80\mu\text{l}$ , carrier flow rate  $u=2.48\text{ml/min}$ , tube length  $L=233\text{cm}$  and tube inner diameter  $d=0.5\text{mm}$ . Samples with various  $D_m$  being injected and forwarded by its corresponding carrier, the dispersion coefficient at peak maximum ( $D^S$ ) and residence time ( $Tr$ ) were determined. Results are listed in Table 1.

From Table 1 it can easily be seen that the residence time of samples increase with increasing  $D_m$  of the analyte when the FIA system keeps unchanged.

An aqueous solution of  $2.47 \times 10^{-2}$  M  $\text{CuSO}_4$  in pH=4.5 NaAc-HAc buffer and  $0.78 \times 10^{-3}$  M  $\text{K}_2\text{Cr}_2\text{O}_7$  in pH=4.5 NaAc-HAc buffer were used as sample and reagent to verify the relationship between  $D^S_g$  and  $D^R_g$ . Buffer solution was used to avoid the interference by the formation of pH gradient. The peaks of sample/reagent were recorded as shown in Fig. 5 and Fig. 6.

Table 1 Dispersion coefficient and residence time results obtained of samples with various diffusion coefficients

Sample	carrier	$D_m$ $\times 10^{-5} \text{cm}^2 \text{s}^{-1}$	Tr(s)	$D^3$
$4.56 \times 10^{-3} \text{M K}_3\text{Fe}(\text{CN})_6$ in 1.0M NaOH	1.0M NaOH	0.45 <sup>a</sup>	20.02	2.98
$2.47 \times 10^{-2} \text{M CuSO}_4$ in 0.2M $\text{H}_2\text{SO}_4$	0.2M $\text{H}_2\text{SO}_4$	0.57 <sup>b</sup>	20.20	3.02
$4.56 \times 10^{-3} \text{M K}_3\text{Fe}(\text{CN})_6$ in 1.0M HCl	1.0M HCl	0.76 <sup>a</sup>	20.81	3.08
$4.56 \times 10^{-3} \text{M K}_3\text{Fe}(\text{CN})_6$ in $\text{H}_2\text{O}$	$\text{H}_2\text{O}$	0.96 <sup>c</sup>	20.91	3.13
$6.78 \times 10^{-3} \text{M K}_2\text{Cr}_2\text{O}_7$ in $\text{H}_2\text{O}$	$\text{H}_2\text{O}$	1.24 <sup>c</sup>	21.00	3.23

a: reference 12

b: reference 13

c: reference 14

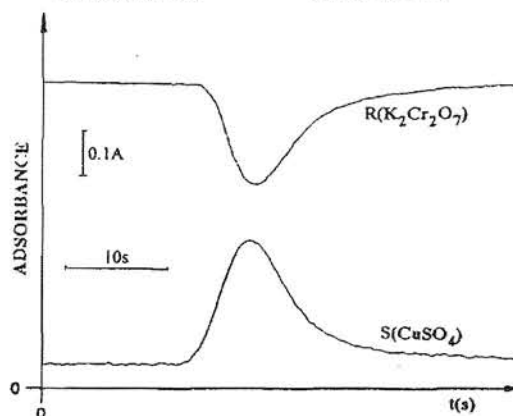


Figure 5 The peak curves obtained with  $\text{CuSO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  as sample and reagent.

$V_{inj} = 80 \mu\text{l}$ ,  $L = 238 \text{cm}$ ,  $d = 0.5 \text{mm}$ ,  $u = 2.48 \text{ml/min}$

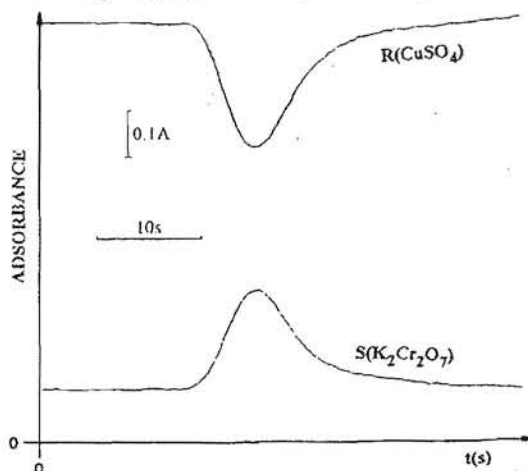


Figure 6 The peak curves obtained with  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{CuSO}_4$  as sample and reagent

$V_{inj} = 80 \mu\text{l}$ ,  $L = 238 \text{cm}$ ,  $d = 0.5 \text{mm}$ ,  $u = 2.48 \text{ml/min}$

In Fig. 5 and Fig. 6,  $D^S=2.944$  and  $Tr=19.700s$  when  $CuSO_4$  was used as sample;  $D^S=3.059$  and  $Tr=19.960$  when  $K_2Cr_2O_7$  was used as sample. Therefore, it is clear that the  $D_m$  of  $K_2Cr_2O_7$  is larger than that of  $CuSO_4$ .

The  $D_g^S$  and  $D_g^R$  at various times selected from Fig. 6 are listed in Table 2 and Table 3.

Table 2  $D_g^S$  and  $D_g^R$  obtained from Fig. 5 ( $CuSO_4$  and  $K_2Cr_2O_7$  as sample and reagent)

$A_g^S$	$D_g^S$	$A_g^R$	$D_g^R$	$1/D_g^S + 1/D_g^R$
0.148	5.73	0.563	1.19	1.015
0.257	3.33	0.480	1.40	1.017
0.284	2.99	0.456	1.47	1.016
0.236	3.59	0.492	1.36	1.103
0.170	4.99	0.538	1.24	1.004
0.109	7.78	0.587	1.14	1.005
0.079	10.73	0.611	1.10	1.006

Table 3  $D_g^S$  and  $D_g^R$  obtained from Fig. 6 ( $K_2Cr_2O_7$  and  $CuSO_4$  as sample and reagent)

$A_g^S$	$D_g^S$	$A_g^R$	$D_g^R$	$1/D_g^S + 1/D_g^R$
0.084	7.98	0.706	1.20	0.958
0.180	3.72	0.597	1.42	0.973
0.219	3.06	0.560	1.44	0.974
0.186	3.60	0.590	1.44	0.978
0.131	5.11	0.653	1.30	0.965
0.084	7.98	0.718	1.18	0.972
0.055	12.18	0.758	1.12	0.976

From Table 2 and Table 3, it can be seen that  $1/D_g^S + 1/D_g^R > 1$  when  $CuSO_4$  was used as sample and  $K_2Cr_2O_7$  was used as carrier, i.e., the sample and reagent were relatively concentrated when smaller  $D_m$  sample was injected into larger  $D_m$  reagent while  $1/D_g^S + 1/D_g^R < 1$  when  $K_2Cr_2O_7$  was used as carrier, i.e., the sample and reagent were relatively diluted when larger  $D_m$  sample injected into smaller  $D_m$  reagent.

Therefore, in a single channel FIA system with the same chemical reaction, the sensitivity obtained by injecting smaller  $D_m$  substance into larger  $D_m$  substance is higher than that

obtained by injecting inversely. In the experiments of Johnson & Petty<sup>1</sup>, rFIA had a higher sensitivity than nFIA just because that the  $D_m$  of  $Mo_7O_{24}^{6+}$  is smaller than that of  $PO_3^{4-}$ .

#### Effect of diffusion coefficient on the double peak shapes in various injection modes

Table 1 indicates that longer residence time is obtained for the sample with larger  $D_m$ . The results listed in Table 2 and Table 3 also indicate that the value of  $1/D_g^S + 1/D_g^R$  obtained before the sample peak maximum is larger than that after the

sample peak maximum. Therefore, in a FIA system with chemical reaction, a double peak with higher rear peak will be obtained by injecting larger Dm sample into smaller Dm reagent while a double peak with higher front peak will be obtained by injecting smaller Dm sample into larger Dm reagent (Fig. 4, Fig. 5).

In order to experimentally test the effect of Dm on the double peak shapes, large injection volume of  $V_{inj}=2\text{ml}$  was used. The FIA system was fixed as flow rate  $u=4.18\text{ml/min}$ , tube length  $L=3.0\text{cm}$ , tube inner diameter  $d=0.75\text{mm}$  and the wavelength of the detector was  $352\text{nm}$ . An aqueous solution of  $6.67 \times 10^{-6}\text{M}$   $\text{KIO}_3$  in  $0.1\text{M}$   $\text{HCl}$  and an aqueous solution of  $0.3\%$   $\text{KI}$  in  $0.1\text{M}$   $\text{HCl}$  were used as sample(reagent) and reagent(sample), respectively.  $0.1\text{M}$

$\text{HCl}$  was added to ensure the pH of the reaction and also to avoid the interference from the formation of pH gradient. The double peaks were recorded as shown in Fig. 7.

As can be seen from Fig. 7, a double peak with higher rear peak was obtained by injecting  $\text{KI}$  into  $\text{KIO}_3$  while a double peak with higher front peak was obtained by injecting  $\text{KIO}_3$  into  $\text{KI}$ . The minus peak obtained by injecting  $\text{KIO}_3$  into  $\text{KI}$  was caused by the presence of iodine formed by air oxidation of iodide in acidic solution.

Since the ion radius of  $\text{I}^-$  ( $3\text{\AA}$ )<sup>15</sup> is smaller than the ion radius  $\text{IO}_3^-$  ( $4\text{\AA}$ )<sup>15</sup> in aqueous solution, the diffusion coefficient of  $\text{I}^-$  is larger than that of  $\text{IO}_3^-$ . Therefore, the double peaks shown in Fig. 7 were obtained.

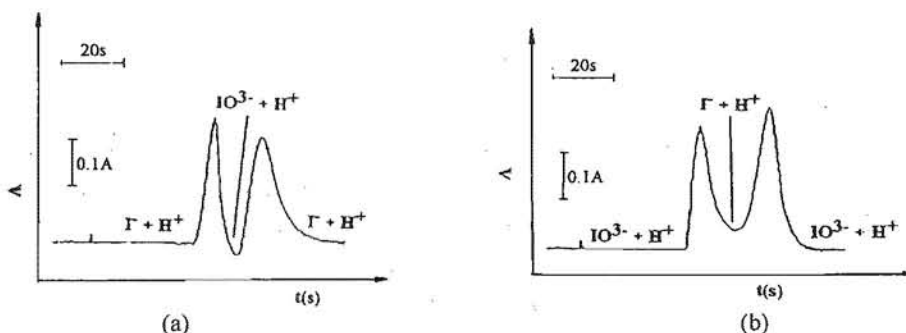


Figure 7 Double peak obtained with  $\text{KI-KIO}_3$  reaction system under different injection modes  
(a)  $\text{KIO}_3$  as injected (b)  $\text{KI}$  as injected

## Conclusions

In this experiment, the differences of sensitivity and peak shapes between two FIA injection modes (nFIA & rFIA) are tested experimentally and

explained with dispersion theory and yields the following conclusions:

1. For a fixed manifold, larger dispersions coefficient and longer residence time will be obtained for



those samples that have larger diffusion coefficient.

2. To a system with the same chemical reaction, the sensitivity obtained by injecting smaller Dm substance into larger Dm substance is higher than that by injecting inversely.
3. For a FIA system with double peaks, the double peak shapes are determined by the diffusion coefficients of the sample and reagent. A double peak with higher rear peak will be obtained by injecting larger Dm substance into smaller Dm substance while a double peak with higher front peak will be obtained by injecting inversely.

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