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Item Type	article;article
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Rights	UMass Amherst Open Access Policy
Download date	2024-08-08 08:18:26
Link to Item	https://hdl.handle.net/20.500.14394/6598

The design of Flow Injection manifolds to give the best detection limits for methods involving on-line chemical derivatisation

Part 2. The spectrophotometric determination of chloride

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The optimisation of a flow injection manifold for the spectrophotometric determination of chloride is described. Factors contributing to the baseline noise due to refractive index and reagent absorption effects are removed by a combination of design features. Firstly, a double-line manifold is used; secondly, pulse-dampers and a packed bed reactor are incorporated into the flow lines and thirdly a delay coil is introduced to resolve the valve switching peaks from the determinand peaks. The appropriate conditions for obtaining the maximum sensitivity are found from an off-line experiment and the guidelines established on the basis of the well-stirred tank model for dispersion applied to the design of the operating parameters of flow rate ratio and volume injected. Good agreement between the predicted and experimentally determined values were obtained. The resulting manifold gave a linear calibration from the detection limit (4.5-8.0 ppb) to 2.00 ppm.

Keywords: *Flow injection analysis, manifold design, chloride determination, double-line manifold, noise, sensitivity.*

The determination of chloride was one of the earliest applications of flow injection analysis (FIA)^{1,2} and several improvements in this method have been reported subsequently³⁻⁸. In these papers more attention was paid to throughput and less consideration was given to maximising sensitivity. The chloride determination suffers from two problems which contribute to the uncertainty in the baseline. The reagent absorbs quite strongly at the analytical wavelength and it has a refractive index considerably different from the determinand carrier stream. This latter feature of the method is one reason why the single line manifold is not used (at low chloride concentrations the refractive index «peaks» completely swamp the product peak). Also the double-line manifold avoids the negative product «peaks» which would be obtained with a single-line manifold at low chloride concentrations. However any inhomogeneity in

the mixing process at and downstream of the confluence point is manifested as baseline noise which is a combination of refractive index and variable absorbance effects.

Previous work has^{9,10} identified the major sources of such noise to be fluctuations in the determinand and reagent stream flow rates due to asynchronous pulsations in the pump channels and incomplete radial mixing in the manifold components downstream from the confluence point. The use of pulse dampers and a combination of packed-bed reactor and open-tubular reactor after the confluence point were shown to be effective in reducing these sources of noise. With this manifold a detection limit for chloride in aqueous solution of 40 ppb was obtained.

The aim of the present study was to optimise the manifold design to achieve the best sensitivity according to the principles previously discussed¹¹ and to minimise further sources of noise. A key concept in the design of manifolds for maximum sensitivity is to establish the appropriate α -value. This parameter is a ratio of concentration ratios and is most readily expressed as the ratio of determinand dispersion coefficient to reagent dispersion coefficient¹² at the peak maximum.

Experimental

Instrumentation

A double-line manifold was constructed from PTFE tubing (0.8 mm and 0.5 mm i.d., Anachem), a Rheodyne 5020 injection valve, a Gilson Minipuls-3 peristaltic pump for pumping carrier and reagent, an LKB Microperpex peristaltic pump for filling the sample loop, packed bed reactors (PBR) (3-7 cm in length, 2 mm i.d., filled with glass beads of 0.3-0.5 mm in diameter), open tubular reactors (OTR) consisting of coils of 0.8 mm i.d. PTFE tubing (0.78-2.32 m in length) coiled tightly around a former 1 cm in diameter and pulse dampers (PD) made from a small glass T-piece and a piece of pump tubing (14 cm in length, 2.8 mm in diameter) stoppered at the end.

The detector was a Pye Unicam SP6-250 visible spectrophotometer with a Pye Unicam 8- μ l quartz flow cell and results were recorded with a Bryans 28000 chart recorder.

Off-line absorbance measurements were made with a Philips PU 8600 uv-visible spectrophotometer in 10 mm disposable plastic cuvettes (Hughes and Hughes Ltd., Romford, England).

Reagents and Solutions

All chemicals used were analytical-reagent grade, and reagent grade water was used throughout. The chloride colour reagent (BDH Ltd) had the following composition: mercuric thiocyanate 0.625 gl^{-1} ($1.97 \times 10^{-3} \text{ M}$), ferric nitrate 30.3 gl^{-1} ($7.5 \times 10^{-2} \text{ M}$), nitric acid 3.3 gl^{-1} ($3.67 \times 10^{-2} \text{ M}$) and methanol 15% (V/V). Chloride standards were prepared by serial dilution of a 100 ppm chloride stock solution, which was made by dissolving 0.164 g of sodium chloride in 1 litre of water. A 0.001% (m/V) aqueous solution of tartrazine (C.I. 19140, BDH, Poole, England) was used to obtain results for the calculation of manifold dispersion coefficients. A 1000 ppm chloride solution (BDH, Poole, England) was used in the off-line studies.

Removal of Valve Switching Effects

A delay coil was inserted between the injection valve and the confluence point. The length of the coil (0.8 mm i.d. OTR) was varied between 10 and 278 cm.

Determination of α -Value

Off-line measurements were made of the absorbance of the reaction product between 2 ppm ($5.64 \times 10^{-4} \text{ M}$) chloride and various dilutions of the reagent. The reactions were carried out in 10 ml calibrated flasks by adding volumes of reagent between 500 and 8000 μl to 20 μl of a 1000 ppm chloride standard solution and making up to volume. The net absorbance was calculated by the subtraction of the absorbance due to a blank solution containing the same concentration of reagent. A curve-fitting software routine (Lab Data Systems, Kirkland Lake, Canada) for a PC-type computer was used in part of the data evaluation.

Investigation of the Effect of Flow Rate Ratio

The linearity of the calibration over the chloride concentration range of 0.1 to 3.0 ppm was investigated for various values of the fractional flow rate due to the determinand carrier stream, f^d . Values of 0.76, 0.80, 0.83 and 0.87 were used.

Investigation of the Effect of Volume Injected

The dispersion coefficient of the manifold was calculated from the peak obtained on the injection of a 0.001% (m/V) aqueous solution of tartrazine.

The peak absorbance obtained for a 0.5 ppm chloride solution was monitored as a function of the volume injected over the range 500 to 2000 μl .

Results and Discussion

Base-line Noise Reduction

The initial manifold design is shown in Fig. 1. The effect of changing the length of PBR and OTR downstream of the confluence point showed that the best results were obtained with a 6 cm PBR and a 1 m OTR. Although the use of a double-line manifold removes the primary refractive index and reagent dilution effects, residual effects were observed at very low chloride concentrations due to valve switching. Valve switching to inject the determinand solution had two effects. The first effect was to halt completely but momentarily the flow of carrier stream. This effect was more marked the slower the valve was switched. The second effect was to increase, when the valve switching was completed, the length of the determinand carrier stream tubing, because it now included the sample loop. This had the effect of slowing the flow rate until such time as the imposed flow rate was restored. It was noticed that changes in pressure during switching of the valve could be followed by observing the changes in the liquid level in the pulse damper. Both of these effects produced increases in reagent concentration reaching the detector which resulted in a temporary increase in absorbance on which was superimposed the first-derivative-shaped refractive index effect. Thus the perturbation of the baseline was caused by two positive absorbance and two refractive index contributions, both of the latter being a sequential positive and negative signal. The combined observed signal usually consisted of a large positive peak followed by a small negative peak.

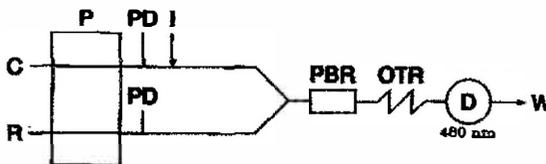


Figure 1. The double-line manifold used initially: C, carrier (water); R, reagent; P, peristaltic pump; PD, pulse damper; I, injection point; PBR, Packed bed reactor; OTR, open tubular reactor; D, detector; W, waste.

When the injection valve was switched back to the «load» position a similar process occurred except that on completion there was a surge of carrier stream owing to the shorter tube length. The observed signal usually consisted

of a twin negative peak composed of a large negative signal due to changes of path length off-set by a central positive signal due to the momentary complete stoppage of flow.

The peaks caused by the valve switching were time-dependent. That is to say, fast injection produced a smaller peak than did slow injection. This in turn resulted in poor reproducibility and degraded the detection limit attainable.

Removal of Valve-Switching effects

The result for the effect of the insertion of different lengths of tubing between the valve and the confluence point are shown in Fig. 2 for the injection of 560 μg of 500 ppb chloride solution. As can be seen from the figure when a delay coil of length 210 cm was used, the switching peak and sample peak are completely resolved.

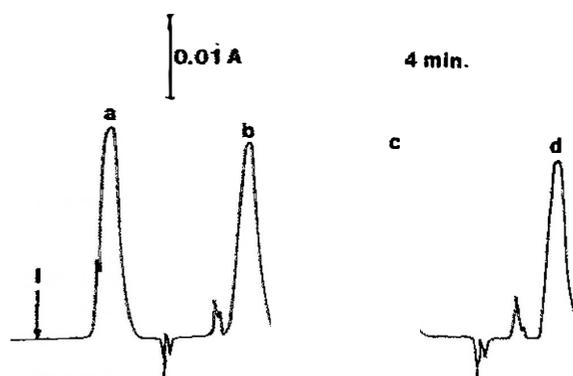


Figure 2. Effect of changing the length of the delay coil: Signals obtained at different delay coil lengths (a) 10 cm; (b) 160 cm; (c) 210 cm; and (d) 278 cm. The manifold shown in Fig. 1 was used with PBR, 6 cm; OTR, 1.0 m; carrier flow rate, 1.80 ml min⁻¹; reagent flow rate, 0.45 ml min⁻¹; sample injection volume, 564 μl ; chloride standard solution, 0.5 ppm.

Determination of α -Value

The results for the variation in the net absorbance for 2 ppm chloride with reagent dilution are given in table 1. The absorbance values are plotted as a function of reagent dilution factor in Fig. 3. The fitted line is the best fit of a quadratic function by an unweighted least squares. The next stage was to treat the data as though they had been produced by a single-line flow injection manifold. Thus the «peak» concentration of the determinand due to physical dispersion was 2 ppm in each case and the reagent dilution factor was equal-

Table 1. Results for the Off-line Formation of Reaction product between a 2 ppm aqueous chloride standard and the reagent at various levels of dilution.

Abs for 2 ppm Cl ⁻	Vol Reagent Taken μ l	Reagent Dilution Factor
0.025	500	20.00
0.031	600	16.67
0.034	700	14.29
0.039	800	12.50
0.056	900	11.11
0.069	1000	10.00
0.073	1500	6.67
0.093	2000	5.00
0.121	2500	4.00
0.130	3000	3.33
0.145	4000	2.50
0.153	5000	2.00
0.159	6000	1.67
0.156	7000	1.43
0.143	8000	1.25

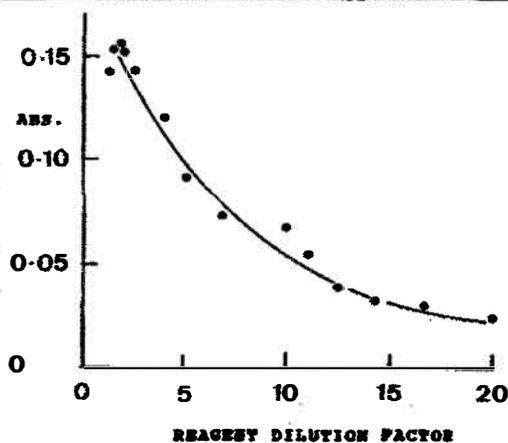


Figure 3. Plot of absorbance for 2 ppm chloride minus absorbance for a blank as a function of reagent dilution factor.

ent to the reagent dispersion coefficient, D^r . As this is related to the determinand dispersion coefficient, D , by the simple relationship $D = D^r / (D^r - 1)$ it is possible to calculate the «injected» concentration of determinand which produced 2 ppm at the peak maximum. Finally the sensitivity of the method was calculated as the ratio of the absorbance to the «injected» concentration and these values plotted as a function of D . This plot is shown in Fig. 4 from which it can be seen that the maximum sensitivity was obtained at a D value of 1.25.

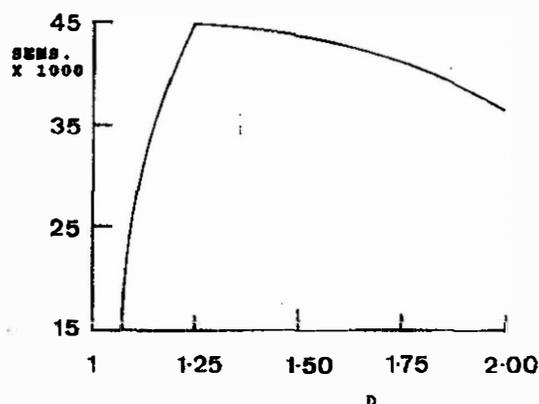


Figure 4. Plot of sensitivity (absorbance divided by «injected» determinand concentration) as a function of determinand dispersion coefficient. The data in Fig. 3 are treated as though they were produced by a single-line flow injection manifold.

It has been calculated previously¹¹ that the required relationship between D and α to obtain the best sensitivity is $\alpha = D - 1$, regardless of whether a single-line or double-line manifold is used and thus the requirement is to obtain an α -value of 0.25 and a D -value of 1.25 for the double-line manifold used here.

Flow Rate Ratio

The theory developed previously¹¹ indicated that to obtain the best sensitivity with a double-line manifold the fractional flow rate due to the determinand carrier stream, f^d , is $(\alpha + 1)^{-1}$ and thus in this case a value of f^d of 0.8 should be selected. The results of the study of the effect of f^d on the shape of the calibration are shown in Fig. 5 from which it can be seen that a value of f^d of 0.8 gives a linear calibration over the range 0.1 - 2 ppm and that there is little difference between this plot and that for $f^d = 0.76$ which corresponds to a D -value of 1.31. This is not inconsistent with the results shown in Fig. 4, which indicate that there is a fairly gentle slope to the plot to the high side of the maximum.

Effect of the Injection Volume

According to the theory described previously¹¹, the value of the volume injected, V_i should be infinite, so that the dispersion effects are due solely to the relative flow rates in the carrier streams. Obviously some practical value

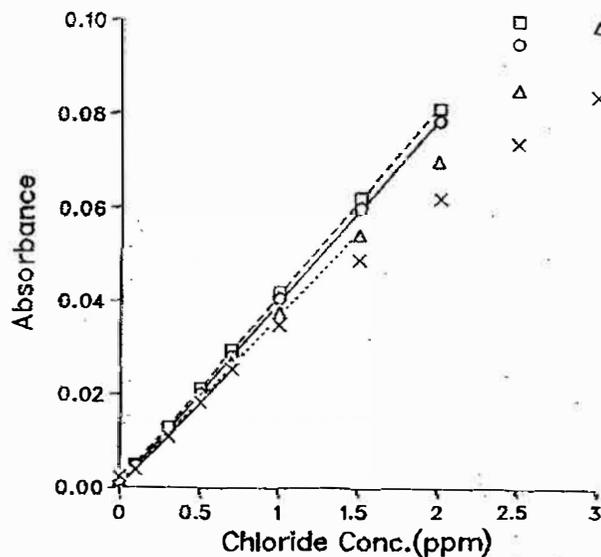


Figure 5. Effect of changing the ratio of carrier stream flow rate to total flow rate (carrier stream flow rate plus reagent stream flow rate): f^d are (O) 0.76, (\square) 0.80, (Δ) 0.83, (X) 0.87. The preliminary manifold was used with PBR, 6 cm; OTR, 1.0 m; total flow rate, 2.25 ml min⁻¹; sample injection volume, 564 μ l.

must be selected to give a D-value sufficiently close to the infinite volume value. To calculate such a volume a value for the hypothetical tank (to which the dispersion effects of the manifold correspond) volume, V, is needed.

The manifold used at this stage contained the delay coil (210 cm) a PBR (6 cm) and an OTR (1 m). The value of f^d was 0.8 and the volume injected was 564 μ l. The dispersion of the injectate of the manifold was monitored using the tartrazine solution and calculated to be 1.29. The appropriate equation, based on the well-stirred tank model¹¹ is

$$D = \{f^d[1 - \exp(-V_i/Vf^d)]\}^{-1}$$

from which the value of V was calculated to be 202 μ l. That is, the manifold behaves as though the peak height of a physically dispersed injectate solution were produced by a combination of plug flow and a single well-stirred mixing tank of volume 202 μ l.

As a compromise between sensitivity and sample throughput, the injection volume required to give 99.8% of the peak height obtained with infinite volume injection was calculated from the above equation. This volume is just over 1 ml. The results of the effect of volume injected on the peak height for a 0.5 ppm chloride solution are shown in Fig. 6. It can be seen that an injection volume of 1 ml is a reasonable value to choose.

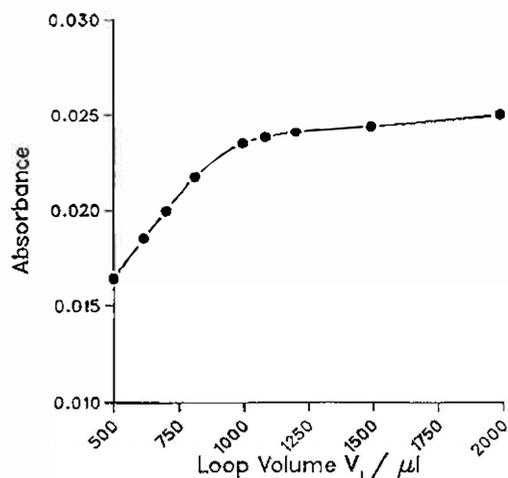


Figure 6. Effect of changing sample injection volume: the manifold described in caption for Fig. 4 was used with a delay coil of 2.1 m in length, 0.8 mm i.d. Chloride standard concentration was 0.5 ppm.

Limit of detection

The final design of manifold is shown in Fig. 7. This manifold was used for the determination of the detection limit for the determination of chloride. The sample carrier stream flow rate was 1.8 ml min^{-1} and reagent stream flow rate was 0.45 ml min^{-1} . The sample injection volume was 1 ml. Chloride standards in the range 0.005 to 0.15 ppm were injected. A chart recorder scale expansion of a factor of 10 was adopted. Typical peaks are shown in Fig. 8 and the corresponding calibration curve in Fig. 9. The detection limit, obtained from the calibration graph¹², for this particular calibration was 5.8 ppb of chloride. Values obtained from 4 different calibrations over a period of 2 weeks ranged from 4.5 to 8 ppb. The correlation coefficients ranged from 0.9917 to 0.9999. The best of the detection limit values is almost an order of magnitude lower than the detection limit reported previously¹⁰.

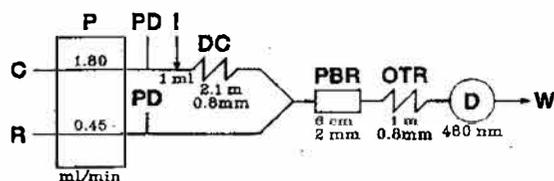


Figure 7. The final manifold design for the determination of chloride at low concentrations: C, carrier, R, reagent; P, peristaltic pump; PD, pulse damper; I, sample injection point; DC, delay coil; PBR, packed bed reactor; OTR, open tube reactor; D, detector, W, waste.

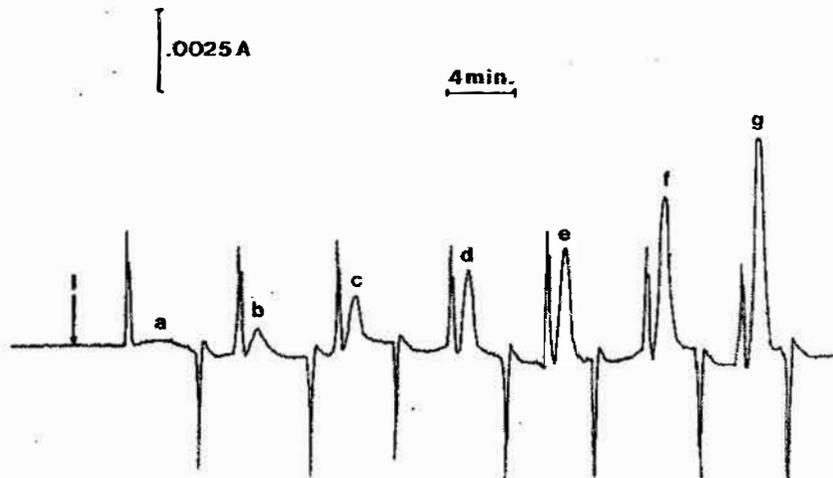


Figure 8. Typical signals obtained when the final manifold was used to determine the detection limit for chloride: a, 0; b, 0.01; c, 0.03; d, 0.05; e, 0.07; f, 0.10; g, 0.15 ppm Cl⁻.

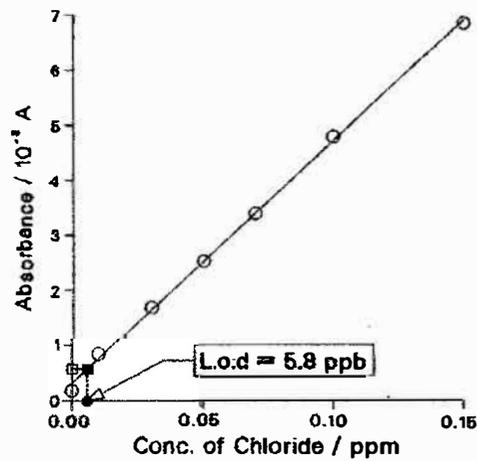


Figure 9. The calibration plot for the determination of the limit of detection for chloride.

Conclusions

Sources of noise in a spectrophotometric procedure arising from the reagent absorbance and refractive index effects can be substantially reduced by the use of a three-stage design procedure. The first step is to use a double-

line manifold rather than a single-line manifold, the second stage is to use pulse dampers and a combination of packed-bed reactors and open tubular reactors to promote mixing downstream of the confluence point and the third stage is to introduce a delay coil between the valve and the confluence point to separate the valve switching peaks from the analytical peaks. The sensitivity may be maximised by adopting the guidelines established from a consideration of the well-stirred tank model for dispersion behaviour. A simple off-line experiment allows the determination of the optimum α -value for the chemistry in question.

ACKNOWLEDGEMENT

The authors thank BDH for the provision of chemicals and the People's Republic of China and Hubei University for financial support and leave of absence, respectively for XW.

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Recibido: 12 de Enero de 1989