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FACTORS AFFECTING THE DETECTION LIMIT OF A FLOW-INJECTION SPECTROPHOTOMETRIC PROCEDURE

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Summary. Design criteria for manifolds to obtain adequate sensitivity and freedom from certain types of noise are discussed. For the determination of chloride by the mercury(II) thiocyanate method, the merging-streams manifold, needed to eliminate negative peaks at low concentrations and refractive index effects, increased the baseline noise because of inefficient mixing at the confluence point. Packed-bed reactors and single-bead-string reactors (SBSR) significantly improved the baseline noise. Refractive index effects caused by sample concentration gradients were eliminated by the injection of large volumes ($> 500 \mu\text{l}$), so that the detector could view a homogeneous central part of the sample zone. This approach maximises the signal because the dispersion is governed only by the relative flow rates of the carrier and reagent streams. The detection limits for chloride were improved to 40 ng l^{-1} in aqueous solutions of low ionic strength and to 1.3 mg l^{-1} in 5.25% (w/v) potassium sulphate.

In any analytical procedure, two factors significantly affect the detection limit: the magnitude of the analytical signal and the magnitude of the noise, which must be maximised and minimised, respectively. In the case of flow injection analysis (f.i.a.), the magnitude of the signal depends on the dispersion in the system, i.e., on the manifold design and operating conditions. Flow-injection solution spectrophotometry usually involves measurement of an increase or decrease in absorbance related to some species which is generated or destroyed by a reaction between the injected sample and a stream of reagent. For measurements based on peak height, it is important to ensure that mixing occurs across the entire sample profile; for this purpose, the manifold must provide such mixing without introducing undue dispersion.

There are several sources of noise in a flow injection system: pump roller noise, mixing noise (arising from incomplete mixing of the carrier and reagent streams) and electronic noise (from the detection and recording devices). Mixing noise, which arises only with manifolds containing confluence points, can sometimes be caused by the peristaltic pump. In addition, the geometry of the confluence point can affect mixing noise and the presence of refractive

index gradients can produce baseline deviations which mask the analytical signal [1].

The reagent used in this study has a density which differs from that of the sample carrier stream, thus simple merging of these two streams produces insufficient mixing. The peristaltic pump used for propelling the streams adds to this problem in that the pump rollers appear to move gradually out of phase. This results in "segmentation" of the two streams causing random, high-frequency, mixing noise. When one pump channel leads on the other, the flow rate in that line surges, so that more of the liquid in the line is merged at the confluence point. The reverse happens when the same channel lags. Thus if one stream absorbs at the detection wavelength, an alternating absorbance will be seen by the detector.

In this communication, methods for maximising the sensitivity and reducing the baseline noise in the spectrophotometric determination of chloride [2] are discussed and evaluated.

Evaluation of manifold design

Manifolds can be of single-line or multi-line design. In the former, a significant contribution to the mixing comes from the interdispersion of sample and reagent caused by the flow patterns in the tubing; in the latter, stream merging at confluence points is the most significant factor in mixing. As this is in addition to any dispersion caused by the flow patterns in the tubing, it might appear that the single-line manifold would be the manifold of choice if maximum sensitivity were the only design criterion. However, preliminary studies [3] have shown that various practical problems are associated with the use of single-line manifolds for chemistries involving reagents such as are used for the determination of chloride.

Two problems arise in the measurement of signals produced from low chloride concentrations. First, because the reagent absorbs at the detection wavelength, the single-line manifold produces a negative peak for concentrations below a certain value; the decrease in absorbance caused by dilution of the reagent is greater than the increase caused by the colour-forming reaction. At the detection limit, the negative peaks produced by the low chloride concentration and by the blank cannot be distinguished. The signal monitoring and processing electronics must be capable of handling negative absorbance values. These negative peaks are not, of course, observed with the merging-stream manifold. The second problem concerns refractive-index gradients. As the mercury(II) thiocyanate/iron(III) reagent contains 15% (v/v) methanol, passage of reagent gradients through the detector causes both negative and positive absorbance peaks to be observed as the gradients refract the light beam. No such reagent gradients exist in the merging-streams manifold, but if the composition of the sample matrix is sufficiently different from that of the carrier stream to produce significant refractive index gradients (as is the case in

the work reported here) then the effect will be observed. One method of overcoming the effect of the gradients at each edge of the sample zone would be to inject such a large sample volume that the detector could view a "central portion" of the sample zone free from concentration gradients. This approach also has the benefit of maximising the sensitivity, as the extent of sample dilution is controlled only by the relative flow rates of the two streams.

A merging-streams manifold requires that each stream is delivered pulse-free and that complete mixing occurs at the confluence point. The use of peristaltic pumps and open tubular conduits has been shown to be less than ideal in this respect [3-5]. Finally, in the determination of trace components in media of high ionic strength (as is the case here), the basic colour-forming reaction can be affected by the decreased activity coefficients.

Experimental

Manifolds. A two-line manifold was used with a variety of components downstream of the confluence point. The Rheodyne model 50 injection valve had a 720- μ l sample loop. The manifold was constructed with PTFE tubing (0.5 mm and 1.0 mm i.d.) and PTFE fittings and connectors. The flow rates of the reagent and sample carrier streams were 2.48 and 0.62 ml min⁻¹, respectively.

Reaction coils were of two distinct types. Open-tube reactors (OTR) consisted of coils (0.5 mm i.d. or 1.0 mm i.d.) tightly wound around a tube of radius 2.5 mm. The second type was either a packed-bed reactor (PBR) [6] or a single-bead-string reactor (SBSR) [7]. Packed-bed reactors were constructed from short lengths of glass tubing (4 cm, 1.5 mm i.d.) filled with glass beads 0.3-0.35 mm in diameter. The SBSRs consisted of lengths of PTFE tubing (0.58 mm i.d.) into which beads of the same size were dry-packed under suction from a water pump; the tubing was coiled tightly around a tube with a radius of ca. 4 mm. To reduce pulsations in the flow, simple pulse dampers were fitted into each line immediately after the peristaltic pump; these pulse dampers consisted of a small glass T-piece, the longer arm of which was stoppered and allowed to fill with air when connected into the manifold.

Confluence points included a Y-shaped (120°) confluence, and a T-piece, both with 0.8-mm bore. Various combinations of manifold elements (i.e., OTRs, PBRs and SBSRs) were investigated. A Visco Jet micro-mixer (Lee Products) was also used as the confluence point; this device contains numerous "spin chambers", in which the two introduced streams are supposedly thoroughly mixed.

Instrumentation. The Cecil Instruments CE273 ultraviolet/visible spectrophotometer was fitted with an 8- μ l quartz flow cell (Hellma). The pump used was a Microperpex digital, stepper-motor peristaltic pump (LKB) equipped with two channels, calibrated by timing the delivery of a known volume of liquid. This value is stored in the pump memory. Peaks were recorded on a Philips model AR-55 linear chart recorder.

Reagents and solutions. All chemicals were of analytical-reagent grade, and triply-distilled water was used throughout. The reagent solution contained mercury(II) thiocyanate (0.625 g l^{-1}), iron(III) nitrate (30.3 g l^{-1}), concentrated nitric acid (3.3 g l^{-1}) and methanol (15% (v/v)). Standards were prepared by serial dilution of a stock solution (1000 mg l^{-1} chloride) of sodium chloride. Samples (analytical-grade potassium sulphate) were prepared as aqueous 5.25% (w/v) solutions.

Removal of refractive index effects. Refractive index gradients were a problem when the potassium sulphate solutions were analysed, because substantial refractive index peaks were observed at the leading and trailing edges of the sample profile. In the initial manifold, a large sample volume was injected, and the refractive index gradients at the edges of the sample profile were outside the field of view of the detector while the centre of the sample zone was in the flow cell. Matrix matching was also possible by using a sample carrier stream having the same concentration as the sample. A solution of AristaR-grade sodium sulphate ($<0.5 \text{ mg kg}^{-1}$ chloride; BDH) was used, the chloride content being included in the baseline. Sample refractive index gradients are then no longer formed. However, the demands placed on the pumping and mixing devices are increased as the differences in physical characteristics between reagent and carrier streams are increased.

Results and discussion

Reduction of baseline noise. The insertion into both lines of the air pulse dampers reduces the amplitude of the baseline noise. The length of the air column was a significant factor; a longer air column produces more effective pulse-damping. The final versions of the pulse dampers used had a length of 13 cm and an internal diameter of 2 mm.

The effects of using the combination of the PBR and wide-bore coiled OTR can be seen in Fig. 1A; the Y-piece confluence was used in these experiments. The baseline noise caused by the pump and poor mixing was much reduced, leading to a decrease in the limit of detection for chloride in water from 1 mg l^{-1} (obtained from previous studies for a single-line manifold) to 40 ng l^{-1} . With the SBSR, it was more difficult to obtain conclusive results. Previously reported studies of reactor performance for the determination of chloride [5] indicated that the SBSR should have been effective in reducing noise. The problem seemed to be that the pump used here was not able to deal effectively with the relatively large back-pressure developed by the SBSR. The use of a PBR alone was not completely effective, but placing the wide-bore OTR (1 mm i.d.) immediately after it gave much better results. Previous evaluations [6–8] of the performance of reactors have concentrated on their contribution to peak broadening rather than their contribution to baseline noise. The PBR (and SBSR) are designed to break the laminar flow pattern so that the flow may approximate to plug flow. However, it would appear that PBRs of the

Fig. 1. (A) Comparison of baselines obtained with various combinations of manifold elements: (a) confluence point only; (b) confluence point and packed-bed reactor; (c) confluence point, packed-bed reactor and 50-cm coiled open tubular reactor. (B) Comparison of the baselines obtained for different confluence-point geometries: (a) Y-piece (120°) confluence and open tubular reactor (1m, 0.5 mm i.d.); (b) T-piece (90°) confluence and open tubular reactor (1m, 0.5 mm i.d.); (c) Visco Jet micro-mixer and open tubular reactor (0.5 m, 1.0 mm i.d.). *A* is absorbance.

dimensions used in this study do not necessarily give rise to uniform mixing and the secondary flow patterns within the stream produced by the tightly coiled OTR are needed to complete the mixing process.

The results of the study of confluence geometry with only OTRs in the subsequent manifold are shown in Fig. 1B, from which it can be seen that, allowing for the different drift, there is little difference between the noise levels produced for the two types of "passive" confluence point. Further work might be done to evaluate the effect of having acute angles between the inlet and outlet of the confluence device, as this configuration has been reported to be particularly efficient at mixing [9]. The performance of the Lee Visco Jet micro-mixer was disappointing (Fig. 1B). Better results were obtained by using a PBR and OTR with the usual Y-piece confluence, although the micro-mixer was more effective than a PBR alone.

When solutions with high ionic strength were injected into a water carrier stream, not only were very large refractive peaks observed, but even the "central" region, where the absorbance was due to iron(III) thiocyanate, showed a decrease in absorbance compared with the baseline until the added chloride concentration exceeded 20 mg l^{-1} . This mode of operation therefore suffered

TABLE 1

Analysis of potassium sulphate by standard additions

Conc. of Cl^- added (mg l^{-1})	0.0	2.0	4.0	6.0	8.0
Absorbance ($\times 10^3$)	3.7	8.8	14.6	17.9	20.9

TABLE 2

Analysis of aqueous solution

Conc. of Cl^- added (mg l^{-1})	0.1	0.2	0.4	0.5	1.0
Absorbance ($\times 10^3$)	2.24	3.02	5.20	6.64	12.6

from a problem similar to one encountered with the use of a single-line manifold at low sample concentrations, i.e., the occurrence of negative peaks.

Matrix matching via the composition of the sample carrier stream was thus preferable for real samples because normal (positive) peaks were obtained; the peak heights were then directly proportional to the chloride concentration and sample throughput could be increased. If necessary, standard additions could be used to improve accuracy. However, irregularities in peak shapes were observed when samples containing chloride were injected into a carrier stream of the same salt concentration but with a different cation. Peaks with large shoulders or double peaks resulted, even though the reagent was in excess over the entire sample profile. This may have been caused by a slight difference in ionic strength because of differences in activity coefficients, which depend on the ionic radii.

A standard additions calibration was used to determine chloride in 5.25% (w/v) potassium sulphate; the results are shown in Table 1. The value of 5.25% (w/v) for the sample and carrier sodium sulphate concentrations was chosen as a compromise between the need to have as great a concentration of contaminant chloride as possible and the effect of high ionic strength on the sensitivity owing to the decreased formation of the iron(III) thiocyanate. The concentration of chloride present from the sample was 2.1 mg l^{-1} . The slope of the line was $2.2 \times 10^{-3} \pm 5 \times 10^{-4} \text{ l mg}^{-1}$; the intercept was $4.5 \times 10^{-3} \pm 2.3 \times 10^{-3}$. The $\pm$ terms are 95% confidence intervals. The correlation coefficient was 0.9903 ($n=5$) and the detection limit [10] was 1.30 mg l^{-1} . Table 2 gives the results for standard additions of chloride to water. The slope of the line was $1.2 \times 10^{-2} \pm 1 \times 10^{-3} \text{ l mg}^{-1}$, and the intercept $7.9 \times 10^{-4} \pm 5.9 \times 10^{-4}$. The correlation coefficient was 0.9987 ($n=5$). The limit of detection was 40 ng l^{-1} .

Conclusion

The best approach to maximising the signal and minimising the noise for a flow-injection spectrophotometric system, in which an absorbing reagent with

refractive index significantly different from that of the sample solution is used, would appear to be the use of a merging stream manifold with injection of a large sample volume. This approach also overcomes problems arising when the refractive index of the sample differs significantly from that of the carrier stream. To avoid the negative peaks which arise when the samples and carrier stream have considerably different ionic strengths, a matrix-matched carrier stream is useful, provided that the level of analyte in the carrier stream can be kept very low. When a merging-streams manifold is used, the pump, confluence point and method of downstream mixing are of crucial importance in obtaining precise results.

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