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A Variable Dispersion Flow Injection Manifold for Calibration and Sample Dilution in Flame Atomic Absorption Spectrometry

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A flow injection (FI) introduction system for flame atomic absorption spectrometry (FAAS) has been constructed for single-standard calibration and sample dilution. Dilution factors ranging from 5.93 to 38.8 in six discrete stages were produced by replicate injection of 12.5- μl volumes into an aqueous carrier stream flowing down lines of different lengths. The dilution factors were measured for five different solutions for each line. No dependence on concentration was found and the relative standard deviations ranged from 0.75 to 3.1%. The manifold was evaluated by the analysis of solutions of magnesium (6, 12.5 and 35 p.p.m.), nickel (180 p.p.m.), calcium (75 p.p.m.) and chromium (180 p.p.m.). Recoveries ranging from 95.3 to 106.8% were obtained with no over-all evidence of bias. The uncertainty in the over-all method, including a contribution from the curve-fitting procedure, was estimated to be 5%.

Keywords: Flow injection analysis; flame atomic absorption spectrometry; calibration; sample dilution

Flow injection (FI) techniques have been used for a wide variety of sample and standard manipulations prior to measurement by flame atomic absorption spectrometry (FAAS).¹ Recent examples of such manipulations include pre-concentration and clean-up using ion exchange,² solvent extraction³ and vapour generation.⁴ Flow injection manifolds for speciation studies⁵ and indirect methods⁶ have also recently been reported. The use of FI techniques for producing solutions for calibration purposes has been described¹ and preliminary results for methods that generate calibration data from a single concentrated standard have been reported.^{7,8} Branched manifolds have been used for dilution purposes for solution spectrophotometry.^{9,10} This paper describes the use of a variable dispersion coefficient manifold that produces six discrete dilution factors for calibration and dilution of off-range samples.

Experimental

Apparatus

A constant displacement pump (Sage Instruments Model 341A syringe pump) was used. With a 30-ml syringe this produced flow ranges covering the nominal range 0.23–8.8 ml min⁻¹ in ten discrete steps. The injection valve was of the rotary type with an external sample loop (Rheodyne Model 5020). The valve was modified by removal of the two connecting tubes to the external loop and substitution of a single length of 0.7 mm i.d. PTFE tubing of volume 12.5 μl . The manifold consisted of six lines in parallel between two six-way switching valves (Rheodyne Model 5011). The dimensions of the lines are given in Table 1. For convenience, the injection and stream-switching valves and six connecting lines were mounted in an enclosed aluminium box. The connections from the box to the atomic absorption spectrometer nebuliser

capillary, was by the minimum length (20.6 cm) of 0.57 mm i.d. PTFE tubing. The complete apparatus is shown in Fig. 1. The spectrometer was a Shandon Southern Model A3300 and the output was monitored with a Philips Model AR55 chart recorder. In all experiments the carrier stream was triply distilled water.

Procedure

Flow-rate effects

The spectrometer was optimised for maximum sensitivity for magnesium and the steady-state and flow injection response measured as a function of flow-rate setting on the pump (2.2, 3.3, 5.5 or 8.8 ml min⁻¹) for a variety of nebuliser capillary positions. A suitable combination of flow-rate setting and capillary position was selected to give an optimum with respect to signal to noise ratio and minimum variation of signal with flow-rate. The flow-rate through each of the six lines was measured by weighing the amount of distilled water carrier delivered to the nebuliser capillary (the connection between the flow injection manifold and instrument being broken at this point to allow convenient collection of carrier stream in a receiving vessel), over an accurately timed interval. The flow-rate in ml min⁻¹ was calculated assuming the specific gravity of water to be unity. Five replicate measurements were made for each line, the means and standard deviations calculated and the results examined for significant differences between the average values.

Dispersion coefficient measurement

A steady-state calibration for magnesium was made over the range 0–1.2 p.p.m. Five solutions of different concentrations were injected for each line. The mean absorbance of the

Table 1. Flow-rates in each line

Line number	Tubing dimensions (length/ cm \times i.d./mm)	Mean rate of flow ($n = 5$)/ml min ⁻¹	Standard deviation/ ml min ⁻¹
1	6 \times 0.7	5.35	0.029
2	18 \times 1.1	5.32	0.028
3	26 \times 1.1	5.41	0.029
4	60 \times 1.1	5.32	0.037
5	131 \times 1.1	5.31	0.057
6	229 \times 1.1	5.33	0.030

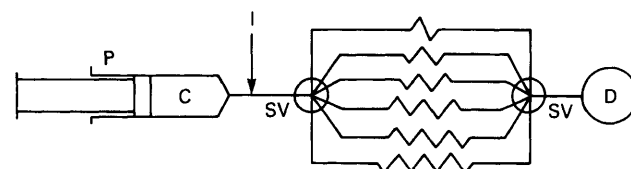


Fig. 1. Schematic diagram of apparatus used. C, Carrier stream (water); D, atomic absorption spectrometer; I, injection valve; P, syringe pump; SV, 6-way switching valve. A detailed description of the apparatus is given in the text

replicate injections for each concentration was calculated and the corresponding concentration found from the calibration plot by interpolation. Division of the original injected concentration by this value yielded a value for the dispersion coefficient. A line of regression of dispersion coefficient on injected concentration was calculated by the method of least squares and the 95% confidence interval for the slope calculated. The mean, standard deviation and 95% confidence interval about the mean of the dispersion coefficient for each line was calculated.

Use of manifold for calibration and dilution of off-range samples

A calibration for magnesium was obtained from a 5 p.p.m. stock standard solution by injection and switching down each of the six lines in turn. Solutions containing 6, 12.5 and 30 p.p.m. of magnesium were analysed by injection down an appropriate line. The concentration corresponding to the peak maximum found from the calibration graph was used to calculate the injected concentration from the known dispersion coefficient value of the line used. The uncertainty in the final calculated value due to the uncertainty of the peak height and of the dispersion coefficient value was calculated. The procedure was repeated with nickel as the test element (calibration obtained from 300 p.p.m., test solution 180 p.p.m.), with calcium (calibration with 100 p.p.m., test solution 75 p.p.m.) and chromium (calibration 250 p.p.m., test solution 180 p.p.m.).

Results and Discussion

Flow-rate Effects

Maximum sensitivity was obtained with the position of the nebuliser capillary set to give the maximum pressure drop along its length and hence the maximum "natural" uptake rate. In agreement with previous studies,⁸ steady-state responses showed a greater variation with flow-rate than did the corresponding FI peak heights. The flow-rate setting of 5.5 ml min⁻¹ on the pump was chosen for all further work as this value fell within a plateau on the peak-height absorbance *versus* flow-rate response curve. The measured flow-rate through each of the six lines is shown in Table 1. Application of the *F*-test shows no significant difference between the variances at the 95% confidence level. Application of the *t*-test shows only one pair of means to have a significant difference at the 95% confidence level namely those for lines 2 and 3. However, there is no evidence that as the line length increases, there is any decrease in flow-rate due to the increased back pressure in the system. It was thus assumed that the response of the spectrometer to any given concentration would be the same regardless of which line was used to deliver the solution to the spectrometer. The independence of flow-rate and tube length will be sustained when the manifold is connected to the instrument due to the negative pressure applied by the nebuliser. This is a feature unique to atomic absorption spectrometers and thus flow-rates essentially independent of tube length may not be obtained with other detectors such as spectrophotometers.

Table 2. Dispersion coefficient measurements for each line

Line number	C_m , p.p.m.	D	Mean D	95% Confidence interval	Standard deviation	Relative standard deviation, %
1	1	6.06	5.93	±0.11	0.091	1.5
	2	5.83				
	3	5.89				
	4	5.98				
	5	5.88				
2	2	9.09	8.67	±0.34	0.27	3.1
	3	8.77				
	4	8.42				
	5	8.47				
	6	8.62				
3	3	10.45	10.35	±0.10	0.078	0.75
	4	10.39				
	5	10.35				
	6	10.26				
	8	10.28				
4	5	15.15	14.87	±0.48	0.39	2.6
	6	14.29				
	8	15.27				
	10	14.93				
	12	14.71				
5	8	26.49	25.99	±0.44	0.35	1.3
	10	25.51				
	12	26.03				
	15	25.86				
	20	26.04				
6	12	40.00	38.84	±0.81	0.65	1.7
	15	38.46				
	20	38.46				
	25	38.64				
	30	38.66				

Dispersion Coefficient Measurement

The dispersion coefficient, D , of a flow injection manifold is defined as $D = C_m/C_p$ where C_m is the injected concentration and C_p is the concentration at the peak. For many FI systems the dispersion coefficient is conveniently measured as the ratio of instrument responses to concentrations C_m and C_p . However, as has been pointed out¹ and discussed in some detail,¹¹ an atomic absorption spectrometer acts as a non-ideal detector. To account for the deviation from linearity of the response - concentration relationship, the response corresponding to the peak maximum is converted into concentration via the steady-state calibration function before calculation of the dispersion coefficient. The results of the measurements of the values of D for each line are given in Table 2. The results for the line of regression calculations are given in Table 3. The data used are those of columns 2 and 3 in Table 2. The 95% confidence intervals for the value of the slopes of the

regression lines include the value 0 for all lines except number 3, and thus the value of dispersion coefficient is taken to be independent of the concentration of the injected solution.

If the response time of the spectrometer was slow compared with the rise time of the FI peak, then it might be expected that the instrument would not follow a large rapid change in concentration at the nebuliser input and thus higher injected concentrations would give rise to an apparently higher dispersion coefficient value. In fact, at first sight, the results obtained suggest an opposite trend as all the regression lines obtained by the least-squares procedure have a negative slope. This would imply that as the injected concentration increased, the measured dispersion coefficient decreases. However, the 95% confidence intervals of the slopes show that this negative value is not statistically significant.

Table 3. Results of regression line calculations

Line number	Slope	$s_{y/x}$ *	Standard deviation of slope	95% Confidence interval
1	-0.02099	0.0983	0.031	0.099
2	-0.1240	0.214	0.058	0.19
3	-0.03621	0.0412	0.011	0.035
4	-0.006098	0.448	0.078	0.25
5	-0.1170	0.405	0.043	0.14
6	-0.04779	0.637	0.044	0.14

* The statistic $s_{y/x}$ is calculated from

$$(n-2) s_{y/x}^2 = \sum (y_i - \hat{y})^2$$

where n is the number of points, y_i is an individual y -value (dispersion coefficient in this instance) and \hat{y} is the y -value of the point on the regression line corresponding to x_i (concentration in this instance).¹²

Table 4. Results of calibration for magnesium; injected concentration 5 p.p.m.

Line number	Dispersion coefficient	Peak absorbance	Standard deviation of absorbance	Calculated concentrations at peak, p.p.m.
1	5.93	0.723	0.010	0.84
2	8.67	0.519	0.014	0.58
3	10.4	0.422	0.009	0.48
4	14.9	0.272	0.007	0.34
5	26.0	0.156	0.002	0.19
6	38.8	0.100	0.005	0.13

Calibration and Dilution

The results for the magnesium calibration based on the injection of 5 p.p.m. down each line are given in Table 4. The calibration data generated were plotted and a curve fitted to the points manually. This curve was used for the analysis of three solutions whose concentrations were well in excess of the top of the conventional calibration range. The results are shown in Table 5. A first estimate of the relative standard deviations (RSD) of the calculated values may be obtained by compounding the RSD values for the absorbance measurements and the dispersion coefficient values. This gives values between 1.5 and 3.2%, which are slightly higher than values obtained from a conventional procedure as the uncertainty in the dispersion coefficient values are greater than in the dilution factor obtained when volumetric glassware is used for dilution purposes.

The calibration data for nickel, calcium and chromium are given in Table 6 and the results for the analysis of off-range solutions of these elements are given in Table 7. An assessment of whether any bias is shown by the method requires an accurate calculation of the uncertainty in the calculated concentration. In addition to the two factors used above, namely the uncertainty in the measured peak height and in the value of the dispersion coefficient, the uncertainty due to the curve-fitting procedure needs to be taken into account. Estimates of the error due to manual curve-fitting procedures have been made,¹³ when it was found that for the elements Mg, Cr and Ni, the value was *ca.* 4%. Thus the over-all uncertainty may be of the order of 5%. To check for bias this value would need to be converted into a 95% (or

Table 5. Analysis of off-range magnesium solutions

Line number	Dispersion coefficient	Peak absorbance	Calculated concentration, p.p.m.	Injected concentration, p.p.m.	Recovery, %
4	14.9	0.342	6.10	6.00	101.7
4	14.9	0.718	12.5	12.5	100.0
5	26.0	0.418	12.4	12.5	99.2
6	38.8	0.732	33.8	35.0	96.6

Table 6. Calibration data for injections of nickel (300 p.p.m.), calcium (100 p.p.m.) and chromium (250 p.p.m.)

Line number	Dispersion coefficient	Peak absorbance	Ni		Ca		Cr	
			Calculated concentration, p.p.m.	Peak absorbance	Calculated concentration, p.p.m.	Peak absorbance	Calculated concentration, p.p.m.	Peak absorbance
1	5.93	0.982	50.6	0.836	16.9	0.502	42.2	
2	8.67	0.862	34.6	0.602	11.5	0.348	28.8	
3	10.4	0.819	28.8	0.510	9.62	0.292	24.0	
4	14.9	0.642	20.1	0.364	6.71	0.203	16.8	
5	26.0	0.423	11.5	0.210	3.85	0.104	9.62	
6	38.8	0.305	7.73	0.154	2.58	0.072	6.44	

Table 7. Analysis of off-range solutions of nickel, calcium and chromium

Element	Line number	Dispersion coefficient	Peak absorbance	Calculated concentration, p.p.m.	Injected concentration, p.p.m.	Recovery, %
Ni	2	8.67	0.675	186	180	103.3
	4	14.9	0.452	186	180	103.3
	6	38.8	0.192	178	180	98.9
Ca	1	5.93	0.691	80.1	75	106.8
	2	8.67	0.470	76.3	75	101.7
	4	14.9	0.264	71.5	75	95.3
	6	38.8	0.110	73.7	75	98.3
Cr	1	5.93	0.371	183	180	101.7
	2	8.67	0.267	191	180	106.1
	3	10.4	0.207	179	180	99.4

similar) confidence interval about the recovery value obtained. It is not possible to do this in a rigorous fashion for the results presented here as no statistically based method of curve fitting was used. However, it can be seen that if the value of 5% is taken as a guide, only one result falls outside $100 \pm 5\%$ recovery. If the contributions to each recovery value are ignored, the mean and its 95% confidence interval calculated for the recovery values as given in the final columns of Tables 5 and 7 are 100.9% and 99.0–102.8%.

Conclusions

It is possible to use a flow injection manifold for on-line dilution for calibration purposes and of sample solutions that are more concentrated than the top standard of a conventional calibration procedure. The method is rapid (after the dispersion coefficients of the manifold lines have been measured), convenient and free from bias. Re-calibration, either of the entire working range or by adjustment of the calibration function based on a single standard may be carried out rapidly. The method is compatible with present computer-based data handling and curve-fitting methods. The precision of the method is poorer than the conventional calibration procedure as the uncertainty in the calculated concentration includes a contribution from the uncertainty in the measured dispersion values. No evidence for these values being dependent on the concentration injected was found and thus no significant contribution from the instrument response function to the over-all dispersion was observed. This may mean that precision could be improved by measurement of the manifold dispersion coefficient values by an alternative technique, such as solution spectrophotometry. With the particular pump used no significant difference in flow-rate down any of the lines was observed and thus the calculated result should be independent of which line is used to produce the sample dilution.

As with all FI-AAS set-ups it is difficult to generalise from the results obtained with one particular combination of flow injection apparatus and AA spectrometer, particularly when

the performance characteristics of the nebuliser are involved. However, the general concept of the variable dispersion coefficient manifold for calibration and dilution should be applicable to all FAA spectrometers.

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