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# Permeation Tubes for Calibration in Flow Injection Analysis

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The use of a permeation tube for the production of liquid stream calibration standards in the flow injection determination of ammonia was investigated. By varying the flow rate from 0.5 to 4.0 ml min<sup>-1</sup>, calibration standards over the range 1.5–0.18 ppm could be produced. The relationship between concentration of the resulting solution and the reciprocal of the flow rate was shown to be linear. The inherent high temperature dependence of the release rate necessitated the tubes being used under thermostated conditions. The release rate was found to vary between 136 and 158 ng min<sup>-1</sup> cm<sup>-1</sup> over a 7 d period. Taking all sources of uncertainty into account, the 95% confidence interval for the release rate varied between 12.0 and 16.2 ng min<sup>-1</sup> cm<sup>-1</sup> over the same 7 d period. The device was used in a manifold for the determination of ammonia in pond water in which the method of standard additions was employed.

**Keywords:** Permeation tube; flow injection; calibration; ammonia determination

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Flow injection (FI) techniques have proved to be useful for the adaptation of a variety of determinations based on aqueous solution reaction chemistry to an automated format. There is considerable interest in the use of FI procedures as the basis of process analysers for on-line monitoring of liquid process streams and waste effluents. A feature of such analysers is the requirement for the production of suitable calibration standards over the relatively long periods of unattended operation.

A number of innovative FI calibration procedures have been described in the past few years.<sup>1–10</sup> Most of these procedures are based on the use of a single concentrated standard from which a set of calibration standards can be produced by a number of dilution procedures that are an inherent feature of the FI dispersion process. Various gradient concentration profiles have been exploited<sup>1–8</sup> for continuous dilution as well as, more recently, the use of a recirculating loop to perform controlled step-wise dilution.<sup>9,10</sup> However, these techniques still require the production of a stock solution on a routine basis and their adaptation to the standard additions format (if needed) is not necessarily straightforward.

In this paper the use of an ammonia permeation tube for calibration of a solution spectrophotometric procedure has been investigated. For the calibration of procedures in which an analyte in a gaseous sample is determined, a range of gas permeation tubes are commercially available (Dynacal permeation tubes, VICI Metronics, Santa Clara, CA, USA). The tubes contain a concentrated solution of the volatile analyte

which diffuses, at a known rate, across the tube walls into an acceptor stream containing a diluent gas. The partial pressure of the analyte is inversely proportional to the acceptor stream flow rate. Thus changing the flow rate of the acceptor stream produces different concentrations of analyte.

There are several reports of the determination of ammonia by FI procedures. Spectrophotometric,<sup>11–13</sup> diffusion<sup>14,15</sup> and various other methods<sup>16–18</sup> have been reported. In this paper a method based on the use of Nessler's reagent was employed.<sup>11</sup>

An important parameter for determining whether these devices are useful for on-line calibration is the day-to-day reproducibility of the release rate at a certain temperature. Ideally the device would be calibrated only once, at the beginning of its life. For release into a gaseous stream, VICI Metronics quotes  $\pm 1\%$  for the first 3–4 months. After that the stability is dependent on the dryness of the gas used and can vary by up to  $\pm 5\%$ . It is likely that over the lifetime of the tube (estimated as 7 months) stability will not be as good because of the release into aqueous solutions. Day-to-day reproducibility of the release rate was investigated along with the variation of release rate with temperature.

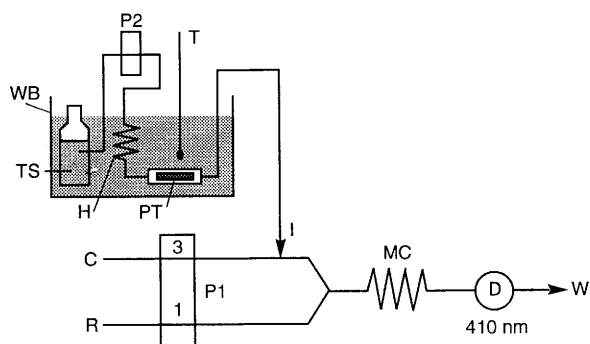
## Experimental

### Apparatus

The manifold (see Fig. 1) was constructed from 0.8 mm i.d. Teflon tubing (Omnifit, New York, NY, USA), polyethylene ethyl ketone (PEEK) nuts and ferrules (UpChurch Scientific, Oak Harbor, WA, USA), and Teflon unions (Omnifit). A six-port rotary injection valve (PhaseSep, Norwalk, CT, USA) with 0.8 mm i.d. Teflon tubing connections was used for

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**Fig. 1** Schematic diagram of the manifold used for the determination of ammonia with Nessler's reagent. Components are as follows: variable speed peristaltic pumps, P1 and P2 (numbers are approximate flow rates in  $\text{ml min}^{-1}$ ); injection port, I; 25 cm mixing coil, MC; detector, D; waste, W; carrier stream, C; Nessler's reagent, R; tube stream solution, TS; permeation tube, PT; 1.5 m heat exchanger coil, H; thermometer, T; and water-bath, WB. Pulse dampers used in each flow line are not shown

sample injection. Reagent, carrier and permeation tube solutions were pumped using two Ismatec MS Reglo variable speed pumps (Cole-Parmer, Chicago, IL, USA) which were fitted with Tygon pump tubing (Cole-Parmer). The manifold was interfaced to the spectrometer using a 1 cm (18  $\mu\text{l}$ ) pathlength flow cell (Pye Unicam, Cambridge, UK). A Perkin-Elmer chemifold block (Perkin-Elmer, Norwalk, CT, USA) was used to merge the reagent and carrier stream. Pulse dampers were made for each line from a T-piece (Omnifit), a piece of Tygon pump tubing and a pump tube connector (Omnifit) which crimped the Tygon tube at one end.

An ammonia, controlled release, Dynacal permeation tube with an active length of 5 cm (6 mm o.d.) (VICI Metronics) was inserted into a 10 cm, 8 mm i.d. glass column (Omnifit) which was fitted with 1/4-28 end-fittings. The permeation device was allowed to rest against the wall of the tube on the rubber seals at each end. The nominal release rate into a gaseous acceptor stream at atmospheric pressure, according to the manufacturer's specifications, was  $295 \text{ ng min}^{-1} \text{ cm}^{-1}$  ( $\pm 10\%$ ) at  $30^\circ\text{C}$ .

For temperature control a water-bath (Fisher Scientific, Pittsburgh, PA, USA) was used in conjunction with a  $22\text{--}28^\circ\text{C}$  thermometer (Emil Greiner, New York, NY, USA) which was accurate to  $\pm 0.01^\circ\text{C}$ .

Real-time data acquisition of the reaction product peaks was obtained using a Lambda 6 UV/VIS spectrophotometer (Perkin-Elmer). The instrument was interfaced to an IBM PS/2 (IBM, Armonk, NY, USA) running Perkin-Elmer Computerized Spectroscopy Software (PECSS) Version 3.26. A Macintosh SE computer (Apple Computer Inc., Cupertino, CA, USA) was used for data evaluation.

Lambda 6 .SP files were converted to .DX files in the PECSS software and then transferred onto Mac using Apple file exchange (Apple). They were then processed using Excel (Microsoft Corp., Redmond, WA, USA) (removal of header and footer) and imported as text into PeaksDemo (Analog Digital Instruments, Milford, MA, USA) for height/area evaluation.

To aid peak identification a 29-point (optimized for this work) median filter recently described<sup>19</sup> was implemented using Excel before files were imported into PeaksDemo.

Each calibration and sample solution was injected five times. Solutions were de-gassed using nitrogen just prior to use as was the solvent used to make up the off-line standards. Any accumulated precipitate was flushed from the manifold by the passage of  $2 \text{ mol l}^{-1}$  hydrochloric acid followed by E-pure water.

Flow rates were calculated by timing the collection of the streams in 10 ml calibrated flasks.

## Reagents and Samples

Nessler's reagent was made up and stored according to the procedure previously described.<sup>20</sup> The potassium iodide, sodium hydroxide and mercury(II) chloride were all of ACS analytical-reagent grade (Fisher Scientific).

Carrier stream and permeation tube stream solutions of  $0.01 \text{ mol l}^{-1}$  nitric acid were made by diluting 0.629 ml of concentrated nitric acid (ACS analytical-reagent grade) to 1 l. Sodium hydroxide carrier stream ( $3 \text{ mol l}^{-1}$ ) was made by dissolving 120 g of solid in 500 ml of E-pure water, transferred to a 1 l flask and made up to volume.

A 100 ppm stock solution of ammonia (as ammonium ion) was made by dissolving 0.3163 g of ammonium chloride (ACS analytical-reagent grade) in 250 ml of  $0.01 \text{ mol l}^{-1}$  nitric acid. Standards were made by appropriate dilution of the stock solution.

De-ionized  $18 \text{ M}\Omega$  E-pure water was used throughout. A sample of water was taken from the University of Massachusetts campus pond and was acidified (pH 2) and filtered ( $0.45 \mu\text{m}$ ) before use.

## Method Development

### Reaction Chemistry

Initial experiments were conducted with an acid-base indicator (Bromothymol Blue) reaction and without temperature control. The majority of the experiments were carried out using Nessler's reagent.

Most of the experimental work was conducted with an acid acceptor stream flowing around the permeation tube. The effects of the variations of flow rate of the acceptor stream and of its temperature were investigated.

### Baseline Noise Reduction

A number of methods for the reduction of baseline noise were investigated, including, the addition of pulse dampers, variation of the mixing device (coil, packed-bed reactor, single bead string reactor, alternating helical reactor and stirred mixing chamber), use of a median filter for post data-acquisition smoothing, and the use of an alkaline acceptor stream.

### Calibration for Ammonia

A series of calibration standards (0.2, 0.5, 1.0 and 2.0 ppm) were prepared off-line and five replicate injections of each solution were made. The solutions were prepared by dilution of the 100 ppm standard made up to volume with  $0.01 \text{ mol l}^{-1}$  nitric acid and were prepared for each calibration of the tube.

The slope of the calibration was calculated by an unweighted least squares procedure for data which did not include a blank value.

### Variation of Concentration With Flow Rate

For four values of the flow rate of the acceptor stream, over the range from approximately  $0.5$  to  $4.0 \text{ ml min}^{-1}$ , five replicate injections of the resulting ammonia solutions were made. The slope of the plot of concentration (obtained from the absorbance *versus* concentration of the standards prepared off-line) *versus* the reciprocal of the flow rate was calculated by an unweighted least squares procedure for data which did not include blank values.

### Calculation of the Release Rate

The release rate of the permeation tube may be calculated from the slope of the concentration *versus* reciprocal flow rate plot, the length of the permeation tube and a conversion factor

for the mass [eqn. (1)]. This gives a result with units that can be compared directly to the manufacturer's nominal value of the release rate into a gas stream.

$$\text{Release rate (ng min}^{-1}\text{ cm}^{-1}\text{)} = \frac{\text{calibration slope } (\mu\text{g min}^{-1}) \times 1000 \text{ (ng } \mu\text{g}^{-1})}{5 \text{ (cm)}} \quad (1)$$

### Variation of the Release Rate With Temperature

The change in release rate as a function of temperature may be calculated from eqn. (2)

$$\log(P_2) = \log(P_1) + \alpha(T_2 - T_1) \quad (2)$$

where  $\alpha$  is  $0.034\text{ }^\circ\text{C}^{-1}$ , and  $P_1$  and  $P_2$  are the respective release rates at  $T_1$  and  $T_2$ . From the data supplied by the manufacturer, it may be calculated that, if the release rate into a liquid acceptor stream is the same as that into a gaseous stream, the release rate would be  $157\text{ ng min}^{-1}\text{ cm}^{-1}$  at  $22\text{ }^\circ\text{C}$ . It can also be seen from eqn. (2) that temperature has a significant effect on the release rate. The release rate changes by approximately 11% for every  $1\text{ }^\circ\text{C}$  increase. Thus a water-bath was used to keep both the permeation tube and the acceptor solution at a steady known temperature for each experiment (see Fig. 1).

A temperature variation study was performed between  $22$  and  $28\text{ }^\circ\text{C}$ .

### Day-to-day Release Rate Variation

An initial study over a period of 1 week showed possible problems. Five experiments performed on different days produced values varying from  $140$  to  $240\text{ ng min}^{-1}\text{ cm}^{-1}$ . Modifications to the manifold were made by: (a) de-gassing the carrier/tube solutions and the water used for the calibration standards; (b) shortening, as much as possible, the tubing out of the water-bath to and from the pump; and (c) adding a heat exchanger coil ( $1.5\text{ m}$ ) after the pump, immersed in the water-bath. This minimized any variation in the dissolved gas concentration in the carrier/tube streams and eliminated the possible heating effect of the pump on the tube solution.

### Analysis of Pond Water Samples

To test that the system worked with real samples,  $500\text{ ml}$  of campus pond water were taken for analysis. Determination of the ammonia concentration was performed using both normal calibration and standard additions (acceptor flow rates of  $0.5$ ,  $1.0$ ,  $2.0$  and  $4.0\text{ ml min}^{-1}$  in both cases). Standard additions is readily performed using the permeation tube as the different additions can be generated by simply passing the sample over the tube at the different flow rates indicated. An unweighted least squares procedure was again used in the calibrations.

## Results and Discussion

### Reaction Chemistry

Initial experiments, performed with nitric acid and Bromothymol Blue, gave peak heights which varied with flow rate as expected. However, significant non-zero intercepts were obtained. This and the non-selectivity of the reaction prompted a change to a quantitative chemical system with selectivity for ammonia. Nessler's reaction was chosen because it has a lower detection limit and faster reaction rate in comparison with the indophenol method.<sup>11</sup>

### Baseline Noise Reduction

Throughout the experimentation significant baseline noise was observed due to the viscosity difference between the Nessler's reagent and the acid carrier stream (which causes difficulties in obtaining rapid radial mixing downstream of the

**Table 1** Peak height *versus* concentration for ammonia solutions

Concentration (ppm)	Peak height (absorbance)
0.20	0.0235
0.50	0.0576
1.00	0.1170
2.00	0.2500

**Table 2** Peak height *versus* reciprocal flow rate for an ammonia permeation tube

(1/flow rate)/ min ml <sup>-1</sup>	Peak height (absorbance)
1.770	0.2700
0.898	0.1307
0.460	0.0710
0.238	0.0380

confluence point), and irregular generation and movement of bubbles through the flow cell. Indeed this is likely to be the reason for the large standard deviation (SD) of the individual results seen in Table 4 as the repeatability of injection of sample and standard solutions was typically poor (5–10%).

An investigation of different mixing devices showed that removal of some of the noise could be achieved. However, this was directly related to an increase in the mixing device volume and thus also resulted in a significant decrease in the sensitivity of the manifold. In addition, the devices did not improve the repeatability of injections and the bubble problem was not removed. The  $50\text{ cm}$  coil used in the experiment provided the best manifold stability albeit with a large amount of baseline noise (standard deviation approximately  $0.01$  absorbance).

Replacing the carrier and acceptor solutions with  $3\text{ mol l}^{-1}$  sodium hydroxide improved the repeatability of injection (3–5%). Also the sensitivity was increased by a factor of 2, due to the elimination of a decrease in the hydroxide concentration at the confluence point. No bubbles were seen which suggests that the bubbles seen in the acid manifold were due to de-gassing of the samples as they were basified at the confluence point (the pH of the resulting solution is over 13).

### Calibration for Ammonia

A typical example calibration for ammonia (Table 1) had a slope of  $0.1255\text{ ppm}^{-1}$  and an intercept of  $-0.005$  with a correlation coefficient of  $0.9993$ . No blank was included in the regression analysis.

### Variation of Concentration With Flow Rate

Plotting peak height *versus* the reciprocal of the flow rate of the acceptor stream gave good linearity in all experiments (typical  $r^2 = 0.999$ ). Table 2 shows a typical calibration with a slope of  $0.1513\text{ ml min}^{-1}$  and an intercept of  $7 \times 10^{-5}$ .

Using the peak heights from this calibration, concentrations of the solutions could be calculated from the off-line calibration. From a plot of concentration *versus* the reciprocal of the flow rate (Fig. 2), it can be seen that the permeation tube shows the same behaviour with a liquid acceptor stream as it does with a gaseous one.

### Calculation of the Release Rate

Taking the slope from the concentration *versus* reciprocal flow rate plot ( $1.20\text{ } \mu\text{g min}^{-1}$ ) the release rate of the permeation tube (and the associated error) can be calculated according to eqn. (1). In this example the release rate was found to be  $240 \pm 23\text{ ng min}^{-1}\text{ cm}^{-1}$ .

### Variation of Release Rate With Temperature

Table 3 shows the results of the release rate variation with temperature. As can be seen the logarithm of the release rate increases linearly with temperature change (compared with the 22 °C value) and the slope is close ( $0.051\text{ }^{\circ}\text{C}^{-1}$ ,  $r^2 = 0.990$ ) to that obtained when using the tube with a gas stream ( $0.034\text{ }^{\circ}\text{C}^{-1}$ ).

### Day-to-day Release Rate Variation

Table 4 shows the results with this modified manifold configuration (Fig. 1) which was the final one used (carrier and acceptor solutions are  $0.01\text{ mol l}^{-1}$  nitric acid). These results are much more reproducible and the average release

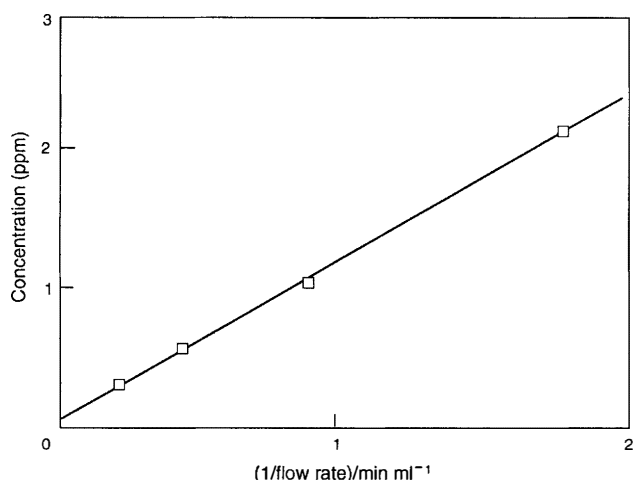


Fig. 2 Concentration versus reciprocal flow rate for ammonia permeation tube,  $y = 0.0396 + 1.2043x$ ;  $r^2 = 0.998$

rate ( $145 \pm 15\text{ ng min}^{-1}\text{ cm}^{-1}$  at 95% confidence) is now closer to the value calculated from eqn. (2). Table 5 shows the results of the same manifold using  $3\text{ mol l}^{-1}$  sodium hydroxide instead of  $0.01\text{ mol l}^{-1}$  nitric acid for the carrier and acceptor solutions. Surprisingly, the release rate ( $153 \pm 22\text{ ng min}^{-1}\text{ cm}^{-1}$  at 95% confidence) is equally as stable with a basic acceptor stream as it is with an acidic one. Indeed, as mentioned before, the repeatability of injection was improved, resulting in the lower standard deviations of the calculated release rates.

### Analysis of Pond Water Samples

Pond water ammonia concentrations using normal calibration were found to be 0.82, 0.69 and 0.71 ppm. Using standard additions the same sub-samples were found to have 0.57, 0.55 and 0.57 ppm ammonia, respectively. This clearly shows the possibility of using these tubes for on-line standard additions calibrations.

### Conclusion

The use of permeation devices for FI calibration has been shown to be a viable proposition provided certain precautions are taken. The most important of these are the stability and control of the temperature of the tube, and the amount of dissolved gases present in the solutions passing across the tube. However, other important considerations should be taken into account. The stability of the pump used has a direct impact on the concentration of the solutions produced. In these experiments, an eight-roller peristaltic pump was used and a pulse damper had to be installed to minimize pulsations caused by the rollers. Transfer line tubing from the end of the permeation tube column to the injection valve was made of Teflon, the same material as the permeation tube. To reduce any possible losses in this part of the manifold it would be advisable to use a material less permeable to gases, e.g.,

Table 3 Variation of release rate with temperature

Temperature/ $^{\circ}\text{C}$	Calibration		Tube solutions		Release rate/ $\text{ng min}^{-1}\text{ cm}^{-1}$		$\Delta T/^{\circ}\text{C}$	Log (release rate)
	Slope	SD	Slope	SD	Value	SD		
22.25	0.1137	0.0034	0.0803	0.0043	141.2	8.7	0	2.150
24.13	0.1137	0.0034	0.1072	0.0069	188.6	13.4	1.88	2.276
26.01	0.1104	0.0052	0.1251	0.0049	226.6	13.9	3.76	2.355
27.97	0.1104	0.0052	0.1555	0.0050	281.7	16.0	5.72	2.450

Table 4 Variation of release rate over a period of days for  $0.01\text{ mol l}^{-1}$  nitric acid carrier and acceptor solutions (using the manifold in Fig. 1)

Day	Temperature/ $^{\circ}\text{C}$	Calibration		Tube solutions		Release rate/ $\text{ng min}^{-1}\text{ cm}^{-1}$	
		Slope	SD	Slope	SD	Value	SD
1	22.08	0.1070	0.0059	0.0789	0.0047	147.5	12.0
2	22.10	0.1082	0.0079	0.0733	0.0044	135.5	12.8
3	22.01	0.1170	0.0068	0.0922	0.0055	157.6	13.1
4	22.01	0.1105	0.0095	0.0773	0.0060	139.9	16.2

Table 5 Variation of release rate over a period of days for  $3\text{ mol l}^{-1}$  sodium hydroxide carrier and acceptor solutions (using the manifold in Fig. 1)

Day	Temperature/ $^{\circ}\text{C}$	Calibration		Tube solutions		Release rate/ $\text{ng min}^{-1}\text{ cm}^{-1}$	
		Slope	SD	Slope	SD	Value	SD
1	22.06	0.2160	0.0051	0.1684	0.0103	156.0	10.2
2	22.08	0.2016	0.0065	0.1726	0.0061	171.3	8.2
3	22.01	0.2046	0.0056	0.1447	0.0046	141.4	5.9
4	22.01	0.1988	0.0070	0.1415	0.0110	142.4	12.1

PEEK tubing. The device may also be useful for standard additions calibrations, and it has a wide tolerance to the pH (2–14) of the acceptor stream.

Clearly this approach is only applicable to those analyte species for which a suitable permeation tube is available. The manufacturer's current list of approximately 110 species includes a number that are of relevance to industrial processes such as S<sup>2-</sup>, SO<sub>2</sub>, HCN methanol and ethanol. As a variety of tube lengths are available, the release rate may be selected to allow calibration over a wide range of concentrations.

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