A Low-Cost Light-Scattering Detector for the Flow-Injection Nephelometric Determination of Sulfate

Jaroon JAKMUNEE,^{*1,*2†} Yuthpong UDNAN,^{*1} Richard MORRISON,^{*3} Ronald BECKETT,^{*3,*4}
Ian MCKINNON,^{*3} and Kate GRUDPAN^{*1,*2}

^{*1} Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

^{*2} Institute for Science and Technology Research and Development, Chiang Mai University,
Chiang Mai 50200, Thailand

^{*3} School of Chemistry, Monash University, Clayton, Victoria 3800, Australia

^{*4} Water Studies Centre, Monash University, Clayton, Victoria 3800, Australia

A simple low-cost flow-through light-scattering detector was developed for determining the particle mass concentration in colloidal suspensions. Employing a laser pointer as a light source and a photodiode IC as a light sensor, the detector was shown to have good sensitivity, yet was small and battery operated. The detector was demonstrated to be effective for the flow-injection nephelometric determination of sulfate by precipitation as barium sulfate.

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Introduction

Light-scattering detection has been applied in flow analysis for either the determination of size or mass concentration of particles.¹ Multiangle light-scattering detectors can be combined with particle separation techniques, such as field-flow fractionation (FFF)² and size-exclusion chromatography (SEC),³ for size characterization. The mass concentration of particles can be determined by either multiangle or simple uniaxial detectors.

The determination of a single analyte by uniaxial light-scattering detection in flow injection (FI) and sequential injection (SI) analysis has been widely investigated. Either nephelometric (detection of scattered light at an angle of 90° to the incident beam) or turbidimetric (detection at 0°) methods are usually used. Although turbidity can be easily measured using a spectrophotometer, other phenomena (*e.g.* light absorption or light diffraction) may interfere. Nephelometric measurements are also more sensitive than turbidimetric measurements.

An SI system for the determination of chloride based on precipitation with silver ions has been proposed.⁴ Phosphate can be determined by an SI turbidimetric method based on calcium phosphate precipitation.⁵ A stopped FI turbidimetric immunoassay using the interaction of concanavalin A (antibody) and yeast mannan (antigen) has been investigated.⁶ FI systems based on precipitation reactions have also been widely applied for the determination of drugs, such as thiamine,⁷ promethazine,⁸ amitriptyline,⁹ and chlorhexidine.¹⁰

The determination of sulfate using barium chloride as a precipitating agent has previously been applied in both FI^{11–14} and SI^{15,16} systems. A liquid-drop windowless optical cell has been developed for FI turbidimetric or nephelometric

determination of sulfate by precipitation with barium ion.¹⁷

In this work, a simple and low-cost flow-through light scattering detection system for determining the particle mass concentration was developed. It is based on nephelometric detection, using a laser pointer as a light source and a photodiode IC as a light sensor. The detector was utilized for the flow injection determination of sulfate by precipitation as barium sulfate.

Experimental

Chemicals

Deionized water (Milli Q, Millipore) was used throughout. All reagents were of analytical grade, unless otherwise stated. Sodium sulfate (Merck) was used to prepare a standard sulfate stock solution of 1000 mg SO₄²⁻/L. Solutions of 1.2% w/v BaCl₂ and 0.1% w/v polyvinyl alcohol (PVA) in 0.05 M HCl were prepared from chemicals from Merck. Ethylenediaminetetraacetic acid disodium salt (Na₂EDTA, Merck) was used to prepare 0.2% w/v EDTA. A polystyrene latex bead suspension (particle diameter 0.144 µm) was obtained from Seradyn (IN, USA).

Flow injection apparatus

The flow-injection system used for the determination of sulfate is illustrated in Fig. 1. The system was assembled using a peristaltic pump (FIALab Instruments, USA), a 6-port injection valve (Upchurch Scientific, USA), a 100 cm mixing coil and a flow-through light-scattering cell with a home-built detection system. All connections were made with 0.8 mm i.d. PTFE tubing.

Light scattering detector

A cross-section of the cell is shown in Fig. 2. A perspex plastic block was drilled in order to insert a straight glass tube

† To whom correspondence should be addressed.
E-mail: scijjkmn@chiangmai.ac.th

Fig. 1 Flow-injection nephelometric system for the determination of sulfate. Solutions were 0.2% w/v EDTA (or 0.0060 M) and 1.2% w/v BaCl₂ (or 0.058 M) plus 0.1% w/v PVA in 0.05 M HCl.

Fig. 2 Schematic diagram of the flow-through light scattering cell.

(2 mm i.d.) with o-ring sealing. A light sensor (described below) was mounted at right angles to the tube axis, as shown. A glass microscope cover slide, attached to the block using epoxy glue, acted as a window and sealed the flow-through cell. The block was painted black to minimize any stray light. Finally, the flow cell, the light source and the detector were placed inside a black box

The detection system is depicted in Fig. 3. A red laser diode pointer (680 nm) was used as a light source. A 1.5 V AAA size alkaline battery was sufficient to power the laser diode for at least 3 h. The optical sensor which converts light intensity to voltage was an OPT101W (Burr-Brown Corporation), which has an active area of 2.3×2.3 mm and a peak spectral response at 850 nm, where the responsivity was 0.6 A/W. The useable working range of this detector was 300 nm to 1 μ m.

The OPT101W is housed in a 5-pin, single, in-line package (SIP) containing an integral photodiode and current amplifier. Three external resistors, connected in a "tee" network, were added, as shown in Fig. 3. This configuration¹⁸ results in an effective feedback resistance exceeding 300 MW, giving an effective gain of 3×10^8 V/A. While the frequency response of the detector is significantly reduced when operating at such a high gain, we estimate its value to be about 40–50 Hz, which is more than adequate for the experiments described here. The output of the OPT101W appears as a voltage on pin 5, which was measured by a digital multimeter (Dick Smith Electronics, Australia) interfaced to a computer (Compaq, USA).

Owing to the high circuit gain the input offset current of the OPT101W's internal op-amp produces a small, constant offset voltage (<100 mV) that contributes to the baseline signals in the experiments reported here.

Fig. 3 Light-scattering detector circuit. R1, R2 and R3 are resistors of 3.3 k Ω , 10 M Ω , 100 k Ω , respectively.

Fig. 4 Calibration plot of the detector voltage *versus* the polystyrene (monodisperse 0.144 μ m beads) concentration fitted to a straight line through the origin.

As shown in Fig. 2, the 2.3 mm square detector is positioned 5 mm from the center of the glass tube through which samples flow. This geometry results in the collection of light scattered through the range $90 \pm 40^\circ$. Experiments performed using a much smaller aperture (2 mm) immediately in front of the detector resulted in much weaker signals. The use of a higher powered light source would allow the collection angle to be better defined while maintaining a useful scattering signal.

Procedure for sulfate analysis

A standard or sample (100 μ L) was injected into a stream of 0.2% w/v EDTA pumped at 1.5 mL/min using a peristaltic pump (see Fig. 1), which then passed through a mixing coil to merge with a stream of 1.2% w/v BaCl₂ and 0.1% w/v polyvinyl alcohol (PVA) in 0.05 M HCl before entering the flow-through cell. Light scattering caused by the barium sulfate precipitate was monitored by the detector and recorded on a computer. An FIAGram (a plot of output voltage (linearly proportional to the light scattering intensity) *vs.* time) was obtained for each injection. Data for a series of standard sulfate solutions were plotted (peak height *versus* sulfate concentration), and the resulting calibration graph was used to determine the concentration of sulfate in the unknown water samples.

Results and Discussion

Testing of FI-LSd instrument

A series of 0.144 μ m polystyrene (PS) latex suspensions with concentrations in the range of 2–10 mg/L were injected into the FI system and allowed to flow-through the LS detector. The

Fig. 5 (A) FIagrams obtained with the FIA-LS system shown in Fig. 1 using 100 μ L injections of sulfate of various concentrations. (B) Calibration plot of the detector voltage *versus* the sulfate concentration fitted to a truncated quartic equation, as explained in the text. x^2 = sum of squares of deviations of the points from the line. 95% prediction band such that 95% of the measured points are expected to lie within the band.

maximum difference between replicates of the resulting FIagrams (detector voltage *versus* time) was 10%. The pooled standard deviation between replicates was 1 mV or 2% at the mid-range of the data. The resultant calibration line is plotted in Fig. 4. The data demonstrate the linearity of the detection system. The uncertainty in the slope of the line (the standard error as determined by a least-squares fitting procedure), was $\pm 1\%$.

Flow-injection nephelometric determination of sulfate

Using the FI manifold shown in Fig. 1, the effects of various measurement conditions, concentrations of reagents (EDTA, $BaCl_2$, polyvinyl alcohol), flow rates, injection volume and mixing coil length were studied. From this information the run conditions selected were: Na_2EDTA concentration 0.2% (w/v) or 0.0060 M, $BaCl_2$ concentration 1.2% (w/v) or 0.058 M, PVA concentration 0.1% (w/v), sample injection volume 100 μ L, mixing coil length 100 cm and flow rate for each line 1.5 mL/min.

The carrier stream of alkaline EDTA acts as a wash solution as well as binding some metal ions in the sample.¹⁴ Sulfate reacts with the excess barium ions to form a precipitate before reaching the light-scattering cell. The polyvinyl alcohol would help to stabilize the precipitate by forming a protective layer on the particles.

Table 1 Sulfate contents of natural water samples using the FIA-LS system

Sample	Peak height/V			Sulfate/mg L ⁻¹	
	(i)	(ii)	Mean	Mean	95% confidence
A	0.378	0.362	0.370	30.3	± 3
B	0.614	0.511	0.5625	41.8	± 3
C	1.005	1.14	1.0725	58.7	± 3
D	0.138	0.124	0.131	19.1	± 6
E	0.549	0.491	0.52	34.8	± 3
F	0.189	0.189	0.189	21.1	± 5
G	0.104	0.102	0.103	18.7	± 9

The FIagrams obtained for a series of sulfate injections in the concentration range 10 – 80 mg/L are shown in Fig. 5A. No baseline drift was observed for at least 50 injections. The reproducibility of the peak heights was generally not as good as that for the PS latex sample, with the maximum variation between replicates being 17% and the pooled standard deviation ($f = 5$) over all the samples being 40 mV or 10% at mid-range. This may be due to the variation in the particle size of the precipitate formed, which would affect the scattering of light.¹⁴

The data are plotted in Fig. 5B and are clearly nonlinear. In the absence of any theoretical model for describing the non-linearity, several functions (exponential, sigmoid, polynomial) were evaluated (using the software package Igor Pro¹⁹) for use as an interpolation function. The simplest function that adequately represented the data was a truncated quartic,

$$y = k_2x^2 + k_3x^3 + k_4x^4. \quad (1)$$

The fitted curve is shown in Fig. 5B together with the prediction bands drawn such that 95% of measured points are expected to lie within the band.

The FIA-LS system was then utilized to analyze sulfate in some natural water samples. The reproducibility is similar to that of the sulfate standards: the maximum difference between replicates was 0.1 V or 17% and the pooled standard deviation over all the samples was 0.05 V ($f = 7$).

Using the quartic calibration curve obtained with the sulfate standards, the concentration of sulfate in each natural water was estimated. The results are given in Table 1 together with the 95% confidence limits, determined as follows.

$$95\% \text{ confidence limit} = 0.5 \text{ the width of the } 95\% \text{ prediction band}/(\text{number of replicates})^{1/2} \quad (2)$$

Conclusion

A simple low-cost flow-through light scattering detector was developed for use in FI systems, where precipitates are generated and the resulting turbidity is used as the basis for chemical analysis. The detector employed a readily available laser pointer as a light source and photodiode IC as a light sensor. The detector was tested using polystyrene latex beads and found to be quite sensitive and reliable.

In order to demonstrate the applicability of the LS detector, it was incorporated into an FI system, which was designed to measure the sulfate concentrations using an approach based on the standard turbidimetric method of barium sulfate precipitation. Reasonable results were obtained considering the

known limitations of this method, which result from variations in the particle size of the precipitate. We believe that this method has considerable promise due to the very reproducible mixing conditions that can be obtained in FI systems. Improvements in the accuracy of the analysis should be possible by optimizing the precipitation conditions to obtain more precise control of the particle size. Work is ongoing in our laboratories to produce a method for sulfate analysis which is more precise and efficient than the commonly used batch turbidimetric procedure.

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References

1. S. Ross and I. D. Morrison, "Colloidal Systems and Interfaces", **1988**, John Wiley, New York, 44 – 47.
2. B. Wittgren and K-G. Wahlund, *Carbohydr. Polym.*, **2000**, 43, 63.
3. H. H. Stuting and I. S. Krull, *Anal. Chem.*, **1990**, 62, 2107.
4. R. B. R. Mesquita, S. M. V. Fernandes, and A. O. S. S. Rangel, *J. Environ. Mon.*, **2002**, 4, 458.
5. B. M. Simonet, F. Grases, and J. G. March, *Fresenius J. Anal. Chem.*, **2001**, 369, 96.
6. P. J. Worsfold and A. Hughes, *Analyst*, **1984**, 109, 339.
7. C. O. Costa-Neto, A. V. Pereira, C. Aniceto, and O. Fatibello-Filho, *Talanta*, **1999**, 48, 659.
8. J. M. Calatayud, S. N. Sarrion, A. S. Sampedro, and C. G. Benito, *Microchem. J.*, **1992**, 45, 129.
9. J. M. Calatayud and C. M. Pastor, *Anal. Lett.*, **1990**, 23, 1371.
10. J. M. Calatayud, P. C. Falco, and A. S. Sampedro, *Analyst*, **1987**, 112, 87.
11. I. P. A. Morais, A. O. S. S. Rangel, and M. R. S. Souto, *J. AOAC Inter.*, **2001**, 84, 59.
12. V. Kuban, *Fresenius J. Anal. Chem.*, **1993**, 346, 873.
13. F. J. Krug, E. A. G. Zagatto, B. F. Reis, O. Bahia Filho, A. O. Jacintho, and S. S. Joergensen, *Anal. Chim. Acta*, **1983**, 145, 179.
14. S. Baban, D. Beetlestone, D. Betteridge, and P. Sweet, *Anal. Chim. Acta*, **1980**, 114, 319.
15. R. A. S. Lapa, J. L. F. C. Lima, and I. V. O. S. Pinto, *Analisis*, **2000**, 28, 295.
16. J. F. van Staden and R. E. Taljaard, *Anal. Chim. Acta*, **1996**, 331, 271.
17. H. Liu and P. K. Dasgupta, *Anal. Chim. Acta*, **1996**, 326, 13.
18. J. G. Graeme, "Photodiode Amplifiers", **1995**, McGraw Hill, 25.
19. Igor Pro, Wavemetrics, Inc., Oregon USA.