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## Determination of gaseous sulphur dioxide by capillary isotachopheresis

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### Abstract

An isotachophoretic method is described for the analysis of sulphur dioxide, a major contributor to air pollution and acid rain. Two different sampling procedures are presented: an absorbing bottle equipped with a fritted glass bubbler and a counter-current membrane collection chamber constructed from Kel-F. The sample is collected in a dilute solution of  $\text{H}_2\text{O}_2$  and analysed as sulphate by capillary isotachopheresis (cITP). The limit of detection for the cITP method used was found to be 2.4 ppm. The range of sulphate concentrations analysed by cITP spanned 5–100 ppm; the gas flow-rates used for  $\text{SO}_2$  sampling varied from 170 to 660 ml/min. Good absorbing efficiency is observed for the absorbing bottle sampling system. Initial work on the membrane sampling system is also described. Under the conditions used in this initial study overall limits of detection were 1 ppm  $\text{SO}_2$  for the absorber bottles (with an 80 min sampling time) and 17 ppm for the membrane collection chamber. The method is low-cost, easily operated and needs no sample pre-treatment. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Isotachopheresis; Air analysis; Sample handling; Membranes; Sulphur dioxide

### 1. Introduction

Sulphur dioxide is a major atmospheric pollutant and contributor to acid rain. It also gives intervenial and blade damage in vegetation. It causes bronchoconstriction in both asthmatic and normal individuals at high levels; studies show that ambient levels of  $\text{SO}_2$  are significantly associated with hospital admissions for respiratory conditions and asthma. The presence of  $\text{SO}_2$  in polluted air has an enormous impact on acid rain and acidification of water resources [1,2].

A number of bodies have set standards for atmospheric concentrations of  $\text{SO}_2$ . The European Union values vary depending on the amount of black smoke

present; for example, where there is less than 128  $\text{g}/\text{m}^3$  smoke (determined by the BSI method used in the UK) only 2% of daily means may exceed 131 ppb  $\text{SO}_2$  and member states must take all appropriate steps to ensure that this limit is not exceeded for three consecutive days [3]. World Health Organization health guidelines include 175 ppb as a 10 min mean, 44 ppb as a 24 h mean and 17 ppb as an annual mean [4]. The USA National Ambient Air Quality Standards are 500 ppb as a 3 h mean, 140 ppb as a 24 h mean, and 30 ppb as an annual mean [5].

The standard method to measure  $\text{SO}_2$  is absorption in hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) solution to form sulphuric acid. The resultant acid is determined by acid–base titration. However, the result is subject to interference from other gaseous, acidic or basic

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compounds such as nitric acid and ammonia, respectively [6]. As a result, the reliability of measurements made by titration is reduced and determination of sulphate gives more reliable results. Sulphate can be analysed by ion chromatography [7], however capillary isotachopheresis (cITP) can also offer simple, fast determination. Determinations of other pollutants such as amines in air samples by cITP have been reported [8,9].

This paper describes a method for determination of gaseous sulphur dioxide concentration using capillary isotachopheresis.  $\text{SO}_2$  is absorbed in dilute  $\text{H}_2\text{O}_2$  and analysed as sulphate by cITP. Two different sampling devices for collecting the sample are presented.

## 2. Experimental

### 2.1. Apparatus

A laboratory-built capillary isotachopheresis analyser with an on-column conductivity detector was used throughout the experiments (Fig. 1). It was constructed using an injection valve coupled with a terminating electrolyte reservoir, separation column [90×0.8 mm I.D. fluorinated ethylene-propylene (FEP)] with conductivity cell, isolating transformer and conductivity detection circuit (all from Villa Labeco, Spišská Nová Ves, Slovakia); distribution valves (Omnifit, Cambridge, UK) to connect the separation column to the leading electrolyte reservoir; a ceramic frit (ATI-Russell, Auchtermuchty, UK), introduced into the end of the capillary column, prevented hydrodynamic flow. The injection valve is designed for sample injection and also for connection of the separation column with the waste reservoir to allow of filling the column with electrolyte solutions. In the present study samples were injected using the fixed volume internal sample loop (30  $\mu\text{l}$ ), but a facility is also provided for injection of up to 100  $\mu\text{l}$  using a microsyringe.

The analogue voltage from the conductivity detector was digitised using a LAB PC+ data acquisition card (National Instruments, Austin TX, USA) mounted in a standard personal computer and controlled using LabVIEW, version 4.0 (National Instruments).

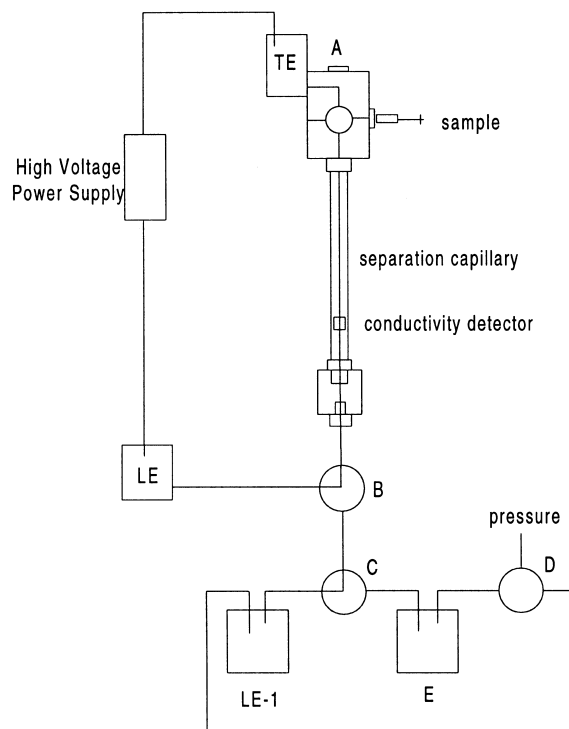


Fig. 1. Schematic diagram of the cITP analyser. LE and TE are leading and terminating electrolyte reservoir, respectively; LE1 is LE reservoir for filling, A is the injection valve, B, C, D are distribution valves; E is the cleaning solution reservoir.

A high voltage power supply (Model EH10R10.0-22, Glassman, Whitehouse Station NJ, USA), which can provide voltages up to 10 kV, was used to drive the separation. The instrument enclosure was equipped with a safety interlock to ensure that the high voltages could only be present when its lid was closed.

### 2.2. Chemicals

The electrolytes used in the separation were similar to those chosen by Zelenský et al. for determination of anions in river water [10]. All chemicals were purchased from Aldrich-Sigma (Poole, UK), were of ultrapure grade and used without further purification.  $\text{SO}_2$  (490 ppm  $\text{SO}_2$  in air) was obtained from BOC (Surrey, UK).

Table 1 lists the composition of the electrolytes used in the isotachopheretic separation.

Table 1  
Electrolyte system used in the experiments<sup>a</sup>

Parameters	Leading electrolyte	Terminating electrolyte
Concentration	HCl, 8 mM	Citric acid, 2 mM
Counter ion	β-ALA	–
Co-counter ion	BTP, 3 mM	–
pH	3.4	3.00
Additive (% w/v)	HEC, 0.2	–

<sup>a</sup> β-ALA = β-Alanine, BTP = bis-tris propane, 1,3-bis-[tris(hydroxymethyl)methylamino]propane, HEC = hydroxyethyl-cellulose.

### 2.3. Air sampling

Two different sampling systems were used for gas sampling. The first system was based on collecting a gas sample into two serial absorbing bottles (Fig. 2). The gas washing bottles were made of glass and equipped with a fritted glass bubbler. Two absorption bottles were used to check the collection efficiency of the system. The flow meter (Platon, Basingstoke, UK) had a range of 100–1200 ml/min.

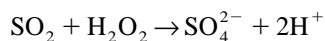
The second system was a counter-current membrane collection chamber constructed from Kel-F. A peristaltic pump (Ismatec, Surrey, UK) was used to pump the collection solution through the system. PTFE thread seal tape with a thickness of 0.076 mm (RS Components, Corby, UK) was used as the membrane. The sampling system and the gas diffu-

sion chamber are shown in Fig. 3a and b, respectively.

## 3. Results and discussion

### 3.1. Isotachophoretic sulphate calibration

As H<sub>2</sub>O<sub>2</sub> was used in the absorbing solution, sulphate was detected on the basis of the following reaction,



Various concentration of sulphates were injected using the 30 μl internal sample loop. Quantitative results were derived from the length of the zones measured from the conductivity data. The initial and recording current of the separation were constant at 100 μA and the typical separation time was 7 min. Examples of conductivity traces for the blank (terminating electrolyte used as the sample) and sulphate solution (20 ppm) are shown in Fig. 4a and b. The relative step height (RSH) for sulphate was calculated to be 0.112 ± 0.012. A calibration graph for sulphate was prepared using standard solutions with concentrations in the range 1–100 ppm. A good linear relationship ( $r^2 = 0.999$ ) with the equation of  $y = 0.929x + 1.45$  is observed. 95% confidence

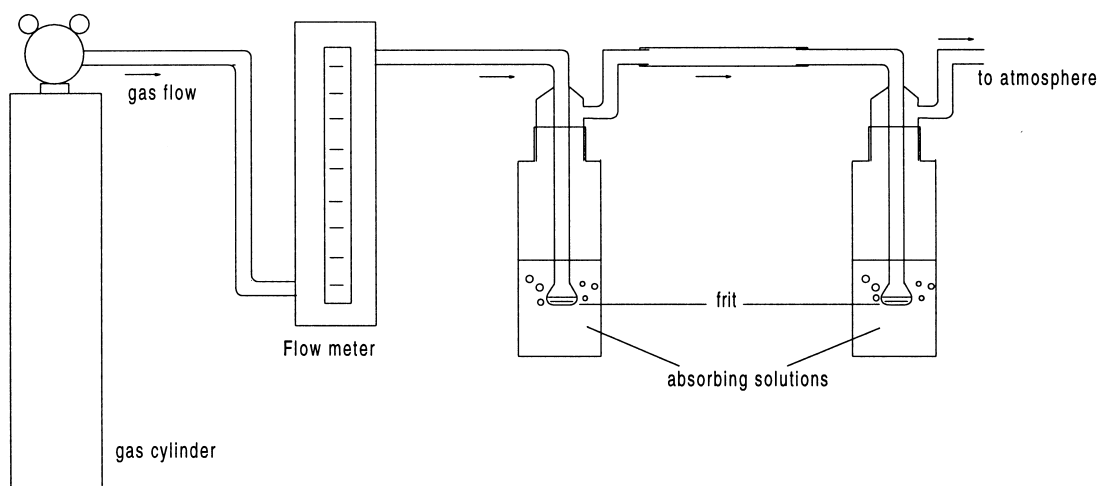


Fig. 2. Absorbing bottles sampling system.

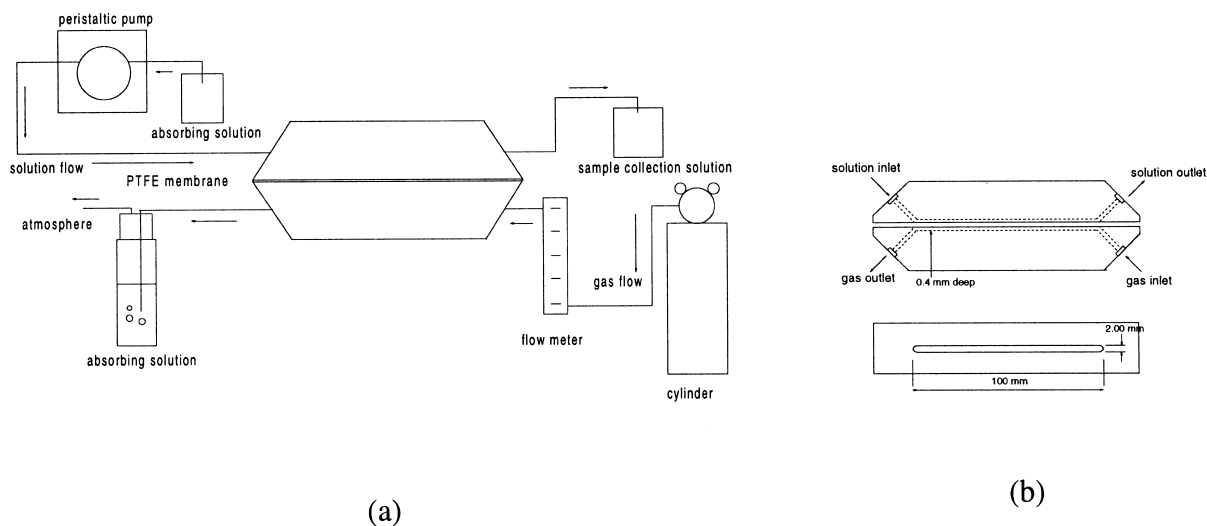


Fig. 3. Sampling system using the counter-current membrane collection chamber. (a) General diagram of sampling system. (b) Gas diffusion chamber.

limits for the slope and intercept were calculated to be  $0.93 \pm 0.015$  and  $1.45 \pm 0.73$ , respectively. The limit of detection was estimated as 2.4 ppm. This compares unfavourably with the thoranol colorimetric method described by Perry and Young [limit of detection (LOD) 0.1 ppm] [11] and the ion chromatography done by Velásquez et al. (LOD 0.044 ppm) [7].

The detection limit could be improved by increasing the injection volume, possible with a microsyringe or by repeated use of the injection valve.

This would give a proportional improvement in sensitivity; standard procedures for the instrument describe the use of 100  $\mu\text{l}$  injections, giving a 3.3-fold improvement. Sensitivity could be improved slightly by decreasing the concentration of the leading electrolyte but at the low pH used this will tend to increase the proportion of the current carried by  $\text{H}^+$  and  $\text{OH}^-$  ions [12], substantial improvement will require different separation conditions, notably essentially neutral pH. This seems feasible, since Zelenský et al. [10] chose a comparatively high

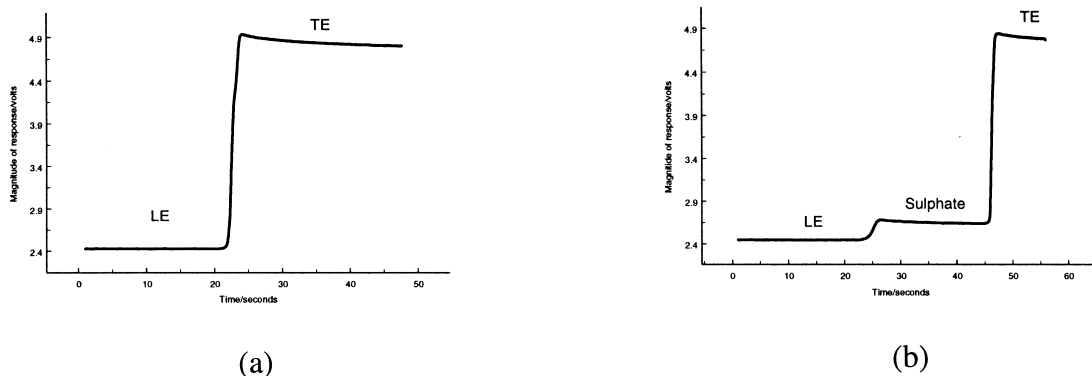


Fig. 4. Isotachopheric separation graphs. LE and TE are the leading and terminating electrolytes, respectively. (a) Blank separation (TE used as a sample). (b) Sulphate (20 ppm) separation.

Table 2  
Absorbing efficiency in the first absorbing bottle at constant flow-rate

	Sampling time (min)							
	1	2	3	4	5	6	8	10
Collection efficiency (%)	80.0	85.6	89.7	91.2	89.4	95.6	95.6	92.5

acidity to separate nitrite from the rest of their sample; in the present case any nitrite will be oxidized to nitrate, so is not expected to interfere.

Both methods will increase sensitivity to trace contaminants in the collection water and equipment, which may migrate with the sulphate, appearing in the same zone.

### 3.2. Sampling using absorbing bottles

Sampling was performed using two different methods: constant flow-rate and constant sampling time. The second bottle was placed after the first to check the efficiency of the sampling process (Fig. 2). Both bottles contained 75 ml of 0.3% (v/v) H<sub>2</sub>O<sub>2</sub>.

Sampling was first performed at a constant gas flow-rate of 173 ml/min using a range of sampling periods. The solutions from absorbing bottles were analysed using the cITP analyser, giving relative step height of  $0.111 \pm 0.005$ . A statistical *t*-test was carried out between the sulphate calibration and absorbing bottles results to check if the RSH is the same. A *t* value of 0.832 was calculated. The critical *t* (*t*<sub>crit</sub>) value obtained was 2.68 at the 99% confidence level. The calculated *t* value is lower than *t*<sub>crit</sub> for these experiments, so it is statistically safe to say that the RSH of the sulphate zones obtained during the calibration and from the absorbing solutions are equal, and hence we may assume that complete separation of the absorbing solution was achieved.

The relationship between the sampling time and determined sulphate concentration is linear. The

equation of the graph was  $y = 4.3x - 0.76$  with an *r*<sup>2</sup> value of 0.998. No sulphate was detectable in the solution from the second bottle.

Table 2 shows the absorbing efficiency, calculated using the cITP experiment results and the calculated gas concentration. The average regression equations were used for both cITP results and gas volume calculation for cylinder concentrations.

SO<sub>2</sub> was also sampled and analysed using different gas flow-rates with the sampling time fixed at 5 min. The relationship between the flow-rate and sulphate concentration was linear ( $y = 0.31x - 6.27$  and *r*<sup>2</sup> = 0.98). Again, no sulphate was found in the second bottle. The absorption efficiency for these experiments is shown in Table 3.

No sulphate was found in the second absorption bottles, indicating near 100% absorption efficiency in the first absorbing bottles. However, the average absorbing efficiencies calculated for the systems were 90 and 95%. This can be validated with the confidence limits of the sulphate and flow-meter calibration regression lines given above. Making the common assumption that SO<sub>2</sub> recovery remains essentially complete down to negligible concentration, taking the absorbent volume used throughout (75 ml) and highest flow-rate used (663 ml/min) together with the limit of detection for the isotachophoretic analysis given above, a limit of detection of the order of 1 ppm could be obtained from an 80 min sample.

Detectability would be improved by the use of higher gas flow-rates. Perry and Young [11] suggest

Table 3  
Absorbing efficiency in the first absorbing bottle using the different gas flow-rates

	Gas flow-rate (ml/min)							
	173	222	271	320	369	467	565	663
Collection efficiency (%)	95.5	96.6	94.5	97.6	91.5	93.2	93.3	96.5

that up to 30 l/min of warm air can be passed through 40 ml of 0.15% (v/v)  $\text{H}_2\text{O}_2$  in a simple bubbler with essentially complete absorption of  $\text{SO}_2$ , and where such high flow-rates are impractical miniature bubblers allow the flow-rate to be reduced in proportion to the reduction in absorbent volume.

It can be said that isotachophoretic determination of  $\text{SO}_2$  after collecting in an absorbing bottle, offers a simple, easily operated and low cost technique.

### 3.3. Counter-current membrane collection apparatus

$\text{SO}_2$  was collected using the apparatus shown in Fig. 3. A PTFE membrane was placed between two halves of the device. The absorbing solution was pumped through the receiving chamber at 1 ml/min using a peristaltic pump. The gas flow was measured using the flow-meter. After sampling, the solution was collected into a bottle and analysed using the cITP analyser. A relative step height value of  $0.117 \pm 0.008$  was calculated. Again a statistical  $t$ -test was carried out between the sulphate calibration and membrane collection systems results to check for equivalent RSH values and hence zone purity. A  $t$  value of 0.058 was calculated. The critical  $t$  ( $t_{\text{crit}}$ ) value obtained was 2.68 at the 99% confidence level. Thus, the calculated  $t$  value is lower than  $t_{\text{crit}}$  for these experiments so it can be said that the RSH values for both systems are equal. As with the

absorbing bottles, this indicates that the separations were complete.

The sampling apparatus was used at a constant gas flow-rate of 222 ml/min and sampling was performed for different periods. The results are shown in Fig. 5. There is no dependence of the sulphate concentration on the sampling time, indicating that diffusion through the membrane is fast.

The results using different flow-rates and a constant 5 min sampling time are given in Fig. 6. The sampling apparatus was then modified so that instead of counter-current, parallel flow is obtained. The results given in Fig. 6 show the absorbing efficiency with parallel flow was not as high as it was for counter-current flow, as would be expected. The relationship between flow-rate and absorption is non-linear; three factors may be involved: the higher partial pressure of  $\text{SO}_2$ ; the higher flow-rate, ensuring that there is little variation in the  $\text{SO}_2$  concentration through the sampler, an improvement enhanced by increased turbulent mixing of the gas; and deformation of the membrane under pressure, reducing its thickness as well as increasing its surface area, both effects can be expected to increase the diffusion rate. A similar relationship between flow-rate and absorption was noticed by Frenzel in a study of a similar absorber [13]. In addition, his study showed decreased efficiency at high flow-rates, this effect would be expected with the present system as well. It is clear from the plot that the concentrations found with flow-rates between 300 and

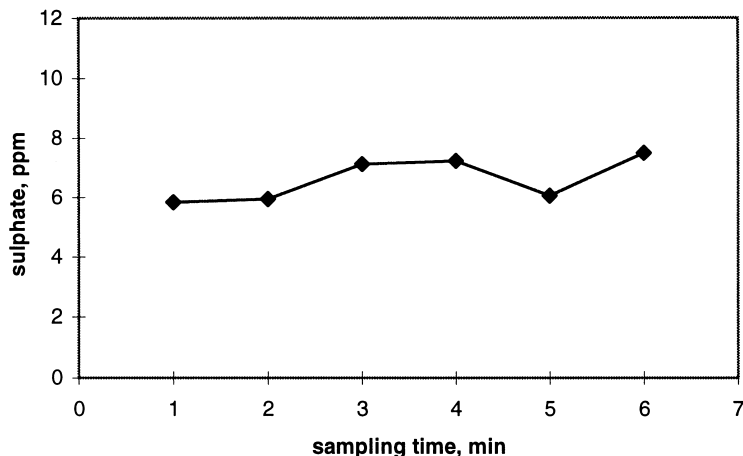


Fig. 5. Results using the counter-current membrane sampling system at constant 222 ml/min flow-rate and different sampling times.

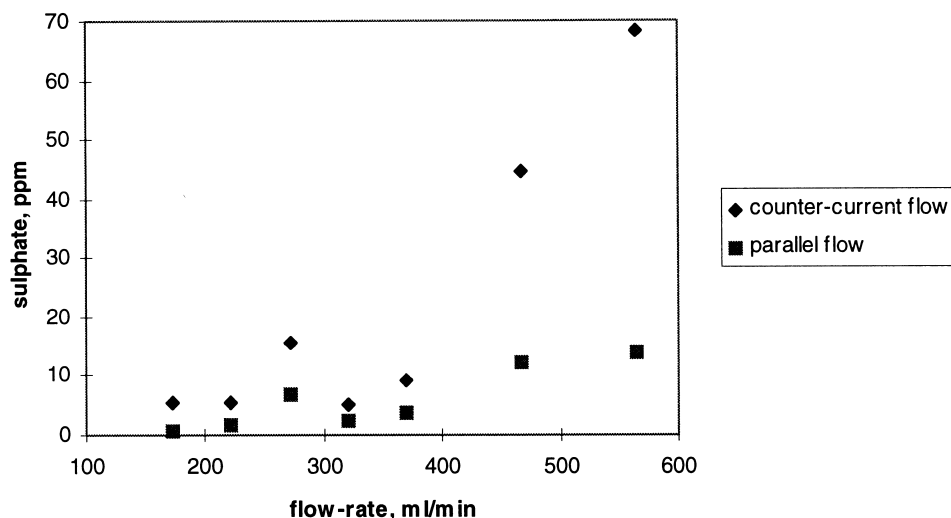


Fig. 6. Results using membrane sampling system with the parallel and counter-current flow.

400 ml/min are anomalously low. Since the behaviour is common to both flow directions it is reasonable to assume that an inexplicable systematic error had occurred and as such, the data should be regarded with caution.

Assuming that sulphate concentration in the absorbing flow is linear with  $\text{SO}_2$  concentration in the gas stream, using this absorber under the most efficient conditions presented here (565 ml/min, counter-current flow) and taking the limit of detection for the isotachophoretic analysis given above, the limit of detection for  $\text{SO}_2$  is 17 ppm. By comparison, if the limit of detection for the absorber bottle system is taken as 1 ppm for an 80 min sample, then 17 ppm would require sampling for approximately 5 min. The efficiency of the membrane sampling system could be enhanced by the use of different membranes, e.g. microporous types such as Gore-Tex or films of silicone rubber, which is known to be highly permeable to many gases. Efficiency would also be improved by reducing the liquid flow-rate and/or recirculating the collection water. Frenzel [13] stopped the flow in his system, and showed that the signal was linear with stoppage period. Both approaches are suitable and likely to give very considerable enhancement since the volume required for injection is less than the volume of the liquid compartment of the absorber.

If, as seems feasible, the sulphate concentration

obtainable can be sufficiently increased then the membrane system becomes the more interesting of the absorbing systems tried, since it can be readily applied to online, continuous, analysis. An automatic ITP analyser with an autosampler and based on a commercial instrument has been presented by Stover et al. [14], but in this case a direct connection to a suitable injection valve is feasible; eluent from the sampler can continuously pass through the injection valve, all that is needed is a capillary-bore overflow to prevent damage when the injection valve is in the inject position. An automatic ITP system based on the laboratory-built system we have reported is currently in preparation for use with this sampler.

#### 4. Conclusion

High sensitivity is needed in systems used for the low level atmospheric pollution measurements, where there is interest in small inexpensive devices, with a short analysis time, for fine-grained surveys. Determination of sulphur dioxide by capillary isotachophoresis after absorbing by  $\text{H}_2\text{O}_2$  solution either in an absorbing bottle or by membrane collection chamber, has been demonstrated. The results of the absorbing bottle system shows that the isotachophoretic analysis of sulphur dioxide is analytically acceptable. However, to be of use an

approximate 1000-fold improvement in sensitivity over the results reported here is required. This does not seem unreasonable since similar absorbing bottles have been shown to work reliably at gas flow-rates 60 times higher (giving a proportional improvement in sensitivity) and recirculating the stripping solution may give a similar improvement with the membrane-based absorber. A 25-fold improvement in detection limit for the analysis stage should be achievable with different electrolytes, particularly if larger injection volumes were used.

The method is easily operated, no pre-treatment of the samples is needed, the analysis time is short and the running cost is low. This method has potential for development into a monitor for atmospheric SO<sub>2</sub> levels and adaptation for use in the determination of a variety of other atmospheric gases.

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