



## Evaluation of ambient SO<sub>2</sub> measurement methods at roadside sites

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### ABSTRACT

Accurate measurements of SO<sub>2</sub> at low ambient concentrations are needed in order to investigate the role of SO<sub>2</sub> in particle nucleation events and the long-term impact of reductions in sulfur emissions in recent decades. In this study, artifacts in SO<sub>2</sub> concentration measurements were investigated using two identical ion chromatography-based instruments (the Gas Particle Ion Chromatograph, GP-IC, Dionex Corporation) and two identical UV fluorescence-based SO<sub>2</sub> analyzers (the TECO 43CTL, an industry standard). The SO<sub>2</sub> concentration values measured with the GP-IC at roadside sites were compared with simultaneous side-by-side measurements made with the fluorescence analyzers. The SO<sub>2</sub> concentration measured with the GP-IC had an ~30% negative calibration artifact. When the GP-ICs were calibrated using an improved procedure developed in the course of this study, only a ±5% difference from the TECO analyzers remained, except under high NO concentration conditions. The fluorescence analyzers exhibited a positive artifact under elevated NO concentration conditions. Sulfur oxidation ratios were calculated based on the GP-IC-measured SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> concentrations and used to help identify potential emission sources. The SO<sub>2</sub> concentrations measured with the GP-IC were also compared to data obtained from a National Air Pollution Surveillance (NAPS) speciation sampler equipped with a Na<sub>2</sub>CO<sub>3</sub>-coated denuder. Good correlation between SO<sub>2</sub> data from the two methods was seen during five months of measurement, but the GP-IC SO<sub>2</sub> data were ~30% lower than the NAPS data. Deposition of SO<sub>2</sub> within an urban street canyon is discussed as a possible explanation for this difference.

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### 1. Introduction

To study gas-particle interactions and gas-aerosol equilibria, a variety of gas-particle instruments based on ion chromatography have been introduced that allow semi-continuous analysis of species of interest in both the gas and the particulate phase. These include the Gas and Aerosol Monitoring System (GAMS), the Wet-Annular Denuder/Steam-Jet Aerosol Collector (WAD/SJAC), the

Dionex Gas Particle Ion Chromatograph (GP-IC), and the Ambient Ion Monitor (AIM) (Loflund et al., 2001; Trebs et al., 2004; Ullah et al., 2006; Wu and Wang, 2007). The Dionex Gas Particle Ion Chromatograph (GP-IC) is a commercial instrument that can measure concentrations of HCl, HNO<sub>2</sub>, HNO<sub>3</sub>, SO<sub>2</sub>, and NH<sub>3</sub> in the gas phase and Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NH<sub>4</sub><sup>+</sup> in PM<sub>2.5</sub> with a 15 min resolution (Dionex Corporation, 2005). In these instruments, ion concentrators are commonly installed upstream of the ion chromatograph. The advantage of using ion concentrators is that it allows injection of a large volume of sample solution (several millilitres), making it possible to analyze low concentration samples. However, this design has the disadvantage that both the injection volume and the concentration of standard solution are required to perform mass calibration of ionic species. Errors in the injection volume of the standard solutions produce equivalent errors in the mass of ionic species measured by the GP-IC (Yao et al., 2009).

Yao et al. (2009) developed a calibration procedure that accurately quantifies the injection volume of the particle channel in the GP-IC. Using the real injection volume significantly reduced the difference

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between particulate sulphate concentrations measured with the GP-IC and those from filter samples, from about 30% to 6–9%. The same magnitude of error (about 30%) caused by the miscalculated injection volume should also appear in GP-IC measurements of gaseous species, although this has not been reported. The calibration procedure first presented in Yao et al. (2009) can be used to quantify the injection volume and thereby eliminate the corresponding artifact in measured SO<sub>2</sub> concentrations. Once this large artifact has been corrected, it is possible to examine other potential artifacts such as the denuder collection efficiency of SO<sub>2</sub>, the conversion efficiency of SO<sub>2</sub> into sulphate, and the particle loss on the denuder.

Kulmala et al. (2004) found that SO<sub>2</sub> gas is the major precursor of nucleation formation of new particles in the atmosphere. When these nucleation events occur in populated regions, they can increase human exposure to ultra fine particulate matter. Accurate measurements of SO<sub>2</sub> in the atmosphere would help to isolate SO<sub>2</sub>-induced nucleation from non-SO<sub>2</sub>-induced particle nucleation events (Shi et al., 2001; Qian et al., 2007). In addition, since sulfur content in fuel and lubricant oil has been reduced in recent decades, accurate measurement of lower ambient SO<sub>2</sub> concentrations has become important for the investigation of the long-term impact of these reductions (Molina and Molina, 2004; Chan and Yao, 2008).

In this study, the injection volume of the gas-side channel of the GP-IC was quantified and the SO<sub>2</sub> concentration was corrected using the actual injection volume. The corrected SO<sub>2</sub> concentration was compared with the concentration measured by two UV fluorescence SO<sub>2</sub> analyzers at different sites. The differences between the data from these two instruments are discussed. Sulfur oxidation ratios were further calculated based on the GP-IC-measured SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> concentrations and used to help identify potential emission sources. In addition, the SO<sub>2</sub> concentrations measured with the GP-IC were compared to data obtained from the National Air Pollution Surveillance network (NAPS) in downtown Toronto. The NAPS data were obtained with a speciation sampler equipped with a Na<sub>2</sub>CO<sub>3</sub>-coated denuder to collect SO<sub>2</sub>. A possible explanation for the ~30% difference is discussed.

## 2. Experimental

### 2.1. Instruments

The Dionex GP-IC combines two high-efficiency wet denuders and a particle collector with two ion chromatographs to measure concentrations of HCl, HNO<sub>2</sub>, HNO<sub>3</sub>, SO<sub>2</sub>, and NH<sub>3</sub> in the gas phase and Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NH<sub>4</sub><sup>+</sup> in PM<sub>2.5</sub> every 15 min. Details of the instrument are provided by Al-Horr et al. (2003), Dionex Corporation (2005) and Godri et al. (2009). This study focussed on artifacts in SO<sub>2</sub> concentrations measured by the GP-IC.

The SO<sub>2</sub> detection method of the GP-IC is described below:

- 1) For the sample: During the 15 min sampling stage, SO<sub>2</sub> gas is collected using a diffusion wet denuder 45 cm in length, with 0.5 mM H<sub>2</sub>O<sub>2</sub> used as the denuder liquid to convert SO<sub>2</sub> into sulphate. The denuder effluent is then sequentially passed through cation and anion concentrator columns. The SO<sub>4</sub><sup>2-</sup> is absorbed by the anion concentrators. During the 15 min analysis period, 15 mM NaOH is used to elute SO<sub>4</sub><sup>2-</sup> captured by the anion concentrator column, and the SO<sub>4</sub><sup>2-</sup> is analyzed directly online using a Dionex ICS-2000 system.
- 2) For the standard: When a calibration is performed, no air is drawn through the denuder. During the 15 min sampling stage, the injection valve switches to loading status to allow loading of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution standards. The injection valve then switches to injection status. The injection loop is used to quantify the injection volume of the standards. During the 15 min analysis

period, the standard is analyzed using the same procedure as applied to the test sample.

Based on the procedure described above, the injection volume of the samples is unknown, but it is much larger than that of the standard. Thus, a mass calibration of sulphate should be performed instead of a concentration calibration. The injection mass of the sulphate in a standard is the product of the injection volume and the sulphate concentration.

Yao et al. (2009) combined two calibration procedures to quantify the volume of standard solution injected into the GP-IC. In Procedure 1, the conventional way to calibrate an ion chromatograph, the standard solution was injected through the fixed volume loops on the GP-IC. In Procedure 2, the particle collector was disassembled from the particle side and connected between the water stream from the gas-side denuder and the injection valve of the gas side. Standard solution of the same concentration was added to the particle collector using an autopipette. Injecting the same mass of a chemical species using Procedure 1 or 2 should cause the same area response, so

$$\text{Area}_{\text{Procedure 1}} / (V_{\text{Procedure 1}} * C_{\text{Procedure 1}}) = \text{Area}_{\text{Procedure 2}} / (V_{\text{Procedure 2}} * C_{\text{Procedure 2}}) \quad (1)$$

where Area<sub>Procedure 1</sub> and Area<sub>Procedure 2</sub> are the area responses for sulphate injected into the GP-IC using Procedures 1 and 2, respectively; V<sub>Procedure 1</sub> and V<sub>Procedure 2</sub> are the volumes of standard injected; and C<sub>Procedure 1</sub> and C<sub>Procedure 2</sub> (μg ml<sup>-1</sup>) are the mass concentrations of sulphate in the standard.

When C<sub>Procedure 1</sub> = C<sub>Procedure 2</sub>,

$$V_{\text{Procedure 1}} = V_{\text{Procedure 2}} / (\text{Area}_{\text{Procedure 2}} * \text{Area}_{\text{Procedure 1}}) \quad (2)$$

Since V<sub>Procedure 2</sub>, Area<sub>Procedure 2</sub>, and Area<sub>Procedure 1</sub> can be measured directly, V<sub>Procedure 1</sub> can be obtained from Eq. (2). A mass calibration using the product of V<sub>Procedure 1</sub> and C<sub>Procedure 1</sub> versus Area<sub>Procedure 1</sub> can then be performed to obtain the proportionality constant K:

$$V_{\text{Procedure 1}} * C_{\text{Procedure 1}} = K * \text{Area}_{\text{Procedure 1}} \quad (3)$$

Thus, the mass of SO<sub>2</sub> diffused through the denuder during sampling can be obtained from

$$\text{Mass of SO}_2 = K * \text{Area}_{\text{samples}} * 64/96 \quad (4)$$

where Area<sub>samples</sub> represents the area response for SO<sub>2</sub> for samples measured by the GP-IC.

### 2.2. Sampling sites

Three sampling sites were selected for comparison of SO<sub>2</sub> concentrations measured by two identical GP-ICs and the SO<sub>2</sub> analyzers. The first sampling site (Toronto West) was located in west Toronto about 190 m from Highway 401 (Fig. 1). This major highway has the highest traffic density in Canada and is heavily travelled by heavy-duty vehicles. Two identical GP-ICs were deployed in two mobile labs parked side by side, 5 m apart, during the measurement period (August 17–28, 2007). They will be referred to as GP-IC-UoT (University of Toronto) and GP-IC-MoE (Ministry of the Environment). The wet denuder for the gas channel of the two GP-ICs, was connected directly with ambient air using a sampling tube. An SO<sub>2</sub> analyzer (TECO 43CTL) was deployed in a mobile lab and will be referred to as SO<sub>2</sub>-TECO-43c-MoE1. A filter was installed upstream of the gas analyzer. The SO<sub>2</sub> analyzer was calibrated every 6–8 weeks, following the standard calibration procedure. The zero drifting was 0.1 ppbv while the standard deviation was 3%. Daily calibration with an internal permeation source also confirmed the analyzer's stability

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