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Intercomparison of the measurements of oxalic acid in aerosols by gas chromatography and ion chromatography

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Running title: Intercomparison of oxalic acid measurement by GC and IC

Abstract

Oxalate, the anion of oxalic acid, is one of the most abundant measurable organic species in atmospheric aerosols. Traditionally, this bifunctional species has been measured by gas chromatography (GC) after derivatization to butyl ester and by ion chromatography (IC) without derivatization. However, there are few published comparisons of the two techniques. Here, we report the results of an intercomparison study for the measurement of oxalic acid in Arctic aerosols (< 2.5 μm, n=82) collected in 1992 using GC and IC. The concentrations of oxalic acid by GC ranged from 6.5-59.1 ng m^{-3} (av. 26.0 ng m^{-3}, median 26.2 ng m^{-3}) whereas those by IC ranged from 6.6-52.1 ng m^{-3} (av. 26.6 ng m^{-3}, median 25.4 ng m^{-3}). They showed a good correlation (r=0.84) with a slope of 0.96. Thus, observations of oxalate obtained by GC employing dibutyl esters are almost equal to those by IC. Because the accuracy of oxalic acid by GC method largely depends on the method used, it is important to strictly examine the recovery in each study.

Keywords: oxalic acid, gas chromatography, oxalate, ion chromatography, aerosols

1. Introduction

Oxalic acid (C_2) and other low molecular weight dicarboxylic acids are the most abundant organic compound class in atmospheric aerosols from many locations on the globe including urban (Kawamura and Kaplan, 1987; Kawamura and Ikushima, 1993; Yao et al., 2004; Huang et al., 2005; Kawamura et al., 2005; Ho et al., 2007; Aggarwal and Kawamura, 2008; Hsieh et al., 2008; Miyazaki et al., 2009), remote continental (Legrand et al., 2005, 2007; Kundu et al., 2010), coastal (Mochida et al., 2003a; Kawamura et al., 2004) and remote marine (Kawamura and Usukura, 1993; Kawamura and Sakaguchi, 1999; Mochida et al., 2003b; Sempéré and Kawamura, 2003) and polar regions (Li and Winchester, 1993; Kawamura et al., 1996a,b; Kerminen et al., 1999; Narukawa et al., 2003) and are abundantly present in wet precipitation samples (Sempéré and Kawamura, 1994; Kawamura et al., 2001). They account for a few per cent of total aerosol carbon in the urban atmosphere (Kawamura and Ikushima, 1993), and an even larger fraction (up to 16%) in the remote marine atmosphere including the tropics (Kawamura and Sakaguchi, 1999).

Low molecular weight carboxylic acids are water-soluble and thus their presence in aerosols enhance the hygroscopic properties of atmospheric particles (e.g., Saxena and Hildemann, 1996). These compounds in atmospheric particles may enhance their ability to act as cloud condensation nuclei (CCN) or ice nuclei (IN). They are a major fraction of water-soluble organic carbon (WSOC) in aerosols. Oxalic acid is the dominant diacid species in most of the aerosol and wet precipitation samples (e.g., Kawamura and Ikushima, 1993; Sempéré and Kawamura, 1994). Traditionally, two methods have been used for the determination of oxalic acid in aerosols so far; ion chromatography (IC) and gas chromatography (GC). The GC method employing dibutyl ester derivatization has an advantage over the IC technique because it allows the measurement of many diacids from C_2 to over C_{10} in aerosols (e.g., Kawamura and Ikushima, 1993) whereas the IC method generally gives only oxalic acid concentrations (Barboukas et al., 2000).

Presence of both the undissociated form (i.e., oxalic acid) and the dissociated form (i.e., oxalate) are possible in atmospheric aerosols. Both forms are water-extractable. During IC analysis, the sum of oxalic acid and oxalate is determined since oxalic acid is converted to oxalate in the basic eluent. In the GC method, as the derivatization reaction between oxalic acid and BF_3/butanol proceeds, the equilibrium between oxalate and oxalic acid shifts to oxalic acid. Hence, the sum of oxalic acid and oxalate can be quantified in both the IC and GC methods. However, some GC methods (e.g., solvent extraction-based method) reported much lower oxalic acid concentrations. For example, Yang and Yu (2008) reported that oxalic acid concentrations in $PM_{2.5}$ collected in Singapore determined by organic solvent extraction followed by BSTFA derivatization and GC/MS measurement were found to be significantly lower (by about a factor of 15) than those of oxalate determined by IC mehod. When organic solvent extraction/methyl ester derivatization techniques were employed for GC determination, two studies (Grosjean et al., 1978; Satsumabayashi et al., 1990) found that oxalic and malonic acids were not detected and/or substantially underestimated.

Although both GC and IC have been widely used for the determination of oxalic acid in aerosols, there are very few comparisons of the two techniques. Li and Yu (2005) used a modified Kawamura method (Kawamura and Ikushima, 1993) for Hong Kong aerosol samples to compare with IC analysis of oxalate and found a good correlation between the oxalic acid concentrations by the two methods. Considering the limited information on the comparability of these two analytical methods, it is very important to report the result of a detailed intercomparison between IC and GC methods used for the determination of oxalic acid in a large set of aerosol samples. For the comparison, we used lower concentration aerosol samples collected in the Arctic lower troposphere before and after polar sunrise (Barrie, et al., 1994). Several studies have been reported of changes in the organic composition of aerosols during this period when ozone depletion events driven by halogens evolving from heterogeneous

reactions between the atmosphere and frozen snow and ice containing sea salt (Barrie et al., 1994; Kawamura et al., 2005).

2. Methods

Daily size-fractionated aerosol samples were collected from 22 January to 20 April 1992 at the high volume sampler site 500 m from the special studies laboratory at Alert (82.5°N; 62.3°W), the Canadian High Arctic. A high volume virtual impactor sampler (MSP Corporation Model 340) was used with Whatman 41 filters to collect fine (< 2.5 μm) and coarse (> 2.5 μm) particles (Barrie et al., 1994).

Determination of oxalate was performed by ion chromatography. Filters were extracted by adding 12 mL of deionized water (> 18 megaohm resistance) to a vial containing the disk. These samples were then sonicated for 1 hour in an ultrasonic bath and left at room temperature for 48 hours before analysis. If not analyzed immediately, they were refrigerated at 4°C. Samples were analyzed on a Dionex 4500i IC with a 200 μL sample loop. Anions were eluted at a flow rate of 2.0 mL min^{-1} on a Dionex Ionpac AS4A separation column (eluent 1.8 mM Na_2CO_3/1.6 mM $NaHCO_3$) and with an anion micromembrane suppressor using H_2SO_4 as the regenerant. The accuracy of oxalate measurements was better than 10%. Analytical detection limit, defined as 3 times the standard deviation of the baseline noise, was approximately 20 ngL^{-1}.

Filters were also analyzed by GC method for oxalic acid and other water-soluble diacids using the procedure previously reported (Kawamura and Ikushima, 1993; Kawamura et al., 1996a). Briefly, filter aliquots (1/4 for coarse and 3/8 for fine filters) were extracted with organic-free pure water. The extracts were concentrated and then reacted with 14% BF_3/n-butanol at 100 °C for 30 min. to derive carboxyl groups to butyl esters. The butyl esters were extracted with n-hexane and then determined using a gas chromatograph equipped with a split/splitless injector, fused-silica capillary column (HP-5) and flame ionization detector. The

identification of the compounds was performed by a comparison of GC retention times with those of authentic standards. The identification was also confirmed with a GC/MS (ThermoQuest, Voyager) under similar GC conditions. Recoveries of oxalic acid standard spiked to a pre-combusted quartz fiber filter were 79±5%. The recovery increased to 86±6% when oxalic acid was spiked into the real aerosol sample (Kawamura and Yasui, 2005). Duplicate analyses of a few filter samples showed the analytical precision to be better than 10%. Field blank filters that were collected roughly every seven days contained oxalic acid, but concentration levels were less than 10% of aerosol filter samples. The concentrations reported in this paper are corrected for the field blanks, but not for the recoveries.

3. Results and Discussion

A comparison of GC and IC results is given in Table 1 for the concentration ranges and average concentrations of oxalic acid in fine and coarse modes of aerosol samples (n=82) from Alert. Minimum, maximum and average concentrations are similar between two methods. In fine mode aerosols (< 2.5 μm), the average concentration of oxalate by IC (26.6 ± 9.5 ng m^{-3}) is not significantly different from that by GC (26.0 ± 9.7 ng m^{-3}). On the other hand, coarse mode aerosols showed that the average concentration of oxalic acid (1.75 ± 1.60 ng m^{-3}) obtained by GC is lower by 11% than that (1.96 ± 1.26 ng m^{-3}) by IC (Table 1). Less agreement for coarse mode particles may be caused by the very low concentrations of oxalic acid in the coarse mode: more that 90% of total oxalic acid is present in fine mode particles.

Concentrations of oxalate (IC) and oxalic acid (GC) in the Arctic aerosol samples (fine mode) are plotted in Figure 1. A good correlation was obtained with a correlation coefficient (r) of 0.84 (p-values < 0.0001) and a slope of 0.96 for the regression line. The slope of the regression line is close to unity. This result suggests the concentrations of oxalic acid obtained by IC and GC are highly comparable. Similar results were obtained for Hong Kong aerosols (r=0.848 and the slope of regression line to be 1.03) (Li and Yu, 2005), where the butyl ester

derivatization technique used was modified from Kawamura and Ikushima (1993). These results indicate that oxalic acid concentrations obtained by butyl ester/GC method are consistent with those by IC and that the oxalic acid and oxalate data are available to compare each other for various purposes; e.g., to draw the global distributions of oxalic acid in the atmospheric particles.

IC determination of oxalate in aerosols only requires simple sample extraction, filtration and IC injection steps whereas the GC method requires several more complicated steps including sample extraction with pure water, concentration of the extracts, derivatization of the acids to esters and GC injection. For example, during the reaction with BF_3 in n-butanol, oxalate is converted to oxalic acid and then derivatized to butyl ester. These procedures in the GC technique may be the cause of a partial loss of oxalic acid in the process: the recovery is 86%, not 100%. If organic solvent were used for extraction, the recovery of oxalic acid should be significantly lower.

However, the GC method has several advantages over the IC technique. First, with GC the homologous series of dicarboxylic acids (C_2-C_{10}), ketocarboxylic acids, and α-dicarbonyls can be measured (Kawamura et al., 1996a, 2005) whereas the IC method usually measures only oxalate (Barboukas et al., 2000). If a gradient elusion technique is utilized, other species such as malonate and succinate can be determined with IC (e.g., Legrand et al., 2005, 2007). Second, GC is combined on-line to mass spectrometry to obtain mass spectra of various compounds. Using GC/mass spectrometry, we can confirm the identification of GC peaks. This capability allows the identification of unknown organic species, which are still present in the atmospheric aerosols. Third, the GC technique is also available to combine to isotope ratio mass spectrometry via on-line combustion of butyl esters of oxalic and other acids to CO_2 to measure the stable carbon isotope ratios of oxalic acid after the isotope mass balance corrections (Kawamura and Watanabe, 2004). This technique provides additional information

on atmospheric aging of organic aerosols (Wang and Kawamura, 2006; Aggarwal and Kawamura, 2008).

4. Conclusion

This intercomparison of the measurement of oxalic acid and oxalate in size segregated Arctic aerosols by two methods (GC and IC) confirmed that the data by a GC method employing dibutyl esters and IC technique are consistent and the two data sets are available for the comparison of the concentrations. However, the recovery of oxalic acid by the GC method should be strictly examined in each research group in order to obtain the best results.

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Figure Caption

Figure 1. Comparison (n=82) of the concentrations of oxalic acid determined by GC/FID and oxalate determined by IC (correlation coefficient r=0.84, p<0.0001).

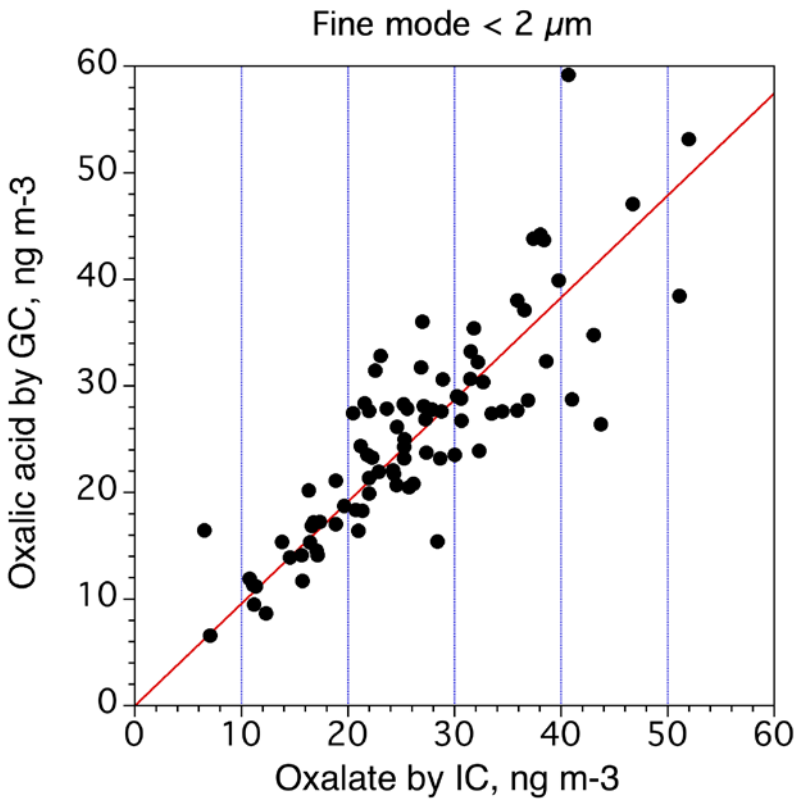

Table 1. Comparison of oxalic acid determination (ngm^{-3}) by ion chromatography (IC) and gas chromatography (GC) employing butyl esters (n=82).

Concentrations, ngm^{-3}	Fine mode < 2.5 μm		Coarse mode > 2.5 μm	
	IC	GC	IC	GC
minimum	6.6	6.5	BDL	BDL
maximum	52.1	59.1	9.37	6.13
average	26.6	26.0	1.96	1.75
standard deviation	9.53	9.71	1.26	1.11
median	25.4	26.2	1.68	1.60

Arctic aerosol samples collected in January to April 1992 were used.