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On-line measurement of perchlorate in atmospheric aerosol based on ion chromatograph coupled with particle collector and post-column concentrator

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ABSTRACT

An automated analysis system has been developed for measuring perchlorate concentration in atmospheric aerosol. The perchlorate in aerosol sample, which has been collected with water mist in a hydrophobic filter/mist chamber based particle collector, is continuously preconcentrated. The matrix ions such as sulfate are subsequently removed from the preconcentrator. The remaining perchlorate is then analyzed on-line with an ion chromatograph in conjunction with a Nafion membrane tube based post-column concentrator. The sensitivity is increased by a factor of 7.7 with the post-column concentration technique. The proposed system has been successfully operated at Tokushima, Japan. The limit of detection is 0.35 ng/m^3 for 3 h sampling cycle. The perchlorate concentration in the atmospheric aerosol averaged 1.01 ± 1.75 ng/m^3 (n=12).

1. Introduction

Perchlorate is highly water soluble and environmentally stable [1,2], leading to the contamination of groundwater and surface water. The concern of human exposure to perchlorate has been spread across the United States since water contaminations by perchlorate were discovered in the lower Colorado River and Lake Mead in 1997 [3]. It is well known that perchlorate, like nitrate and thiocyanate, competitively inhibits iodide transport through the sodium-iodide symporter (NIS) in the thyroid gland [4,5]. Adequate supply of iodide is vital to the function of thyroid and the production of thyroid hormones. Kirk summarized the potential effects of perchlorate intake on neurodevelopment [6]. Recent sensitive methods for perchlorate detection revealed the presence of trace perchlorate in groundwater [7], tap water [8], cow's milk [9], seaweeds [10], vegetables [11], fish [12], and dietary supplements [13]. Two states in the United States have already set a maximum contaminant level for perchlorate in drinking water (2 μg/L for Massachusetts, 6 μg/L for California). In 2011, the United State Environmental Protection Agency (US EPA) decided to regulate perchlorate under the Safe Drinking Water Act (SDWA) [14].

In recent years, the perchlorate contamination has been found in not only the United States but regions across the globe, for example, the Arctic [15], Canada [16], the United Kingdom [17], India [18], China [19], and Korea [20]. Now perchlorate is widely recognized as a worldwide environmental issue. In Japan, perchlorate in drinking water sources of metropolitan area was first found in 2006: the maximum concentrations of perchlorate were 340 and 2300 μg/L at the upper Tone River and its tributary, respectively [21]. Dike et al. reported that Japanese cow's milks contained significantly higher levels of perchlorate than those of the United States: 9.4 ± 2.7 (n=54) and 5.9 ± 1.8 μg/L (n=104), respectively [22]. In 2009, the Ministry of Health, Labour and Welfare (MHLW) ranked perchlorate to the Items for Further Study [23]. This category includes 44 items whose toxicities have not been demonstrated, or concentrations in drinking water are not clear. In 2011, based on the Provisional Maximum Tolerable Daily Intake (PMTDI) of 0.01 mg/kg/day by the Joint FAO/WHO Expert Committee on Food Additives (JECFA), the MHLW set a target level for perchlorate in drinking water at 25 μg/L [24].

In the United States, primary sources of perchlorate in the environment are considered (a) oxidizers used as rocket propellants, (b) imported Chilean nitrate fertilizers, and (c) natural productions in the atmosphere. Perchlorate is also used daily in explosive components such as air bag inflators, flares, and fireworks [25]. Dasgupta et al. estimated the strengths of above primary sources are (a) 10.6, (b) 0.75, and (c) 0.13–0.64 Gg/y for

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the United States as a whole [26]. On the other hand, the contribution from the source (c) is expected to be higher in Japan [22]. Limit information is, however, available concerning the perchlorate in the atmospheric aerosol.

The objective of the present study is to develop a continuous measurement system for perchlorate in atmospheric aerosol. Extended period of sampling time is generally required to collect detectable amounts of perchlorate in atmospheric aerosol. Yamada et al. [27] and Handa et al. [28] collected the aerosol samples on a quartz filter for $\sim$1 week, and determined the perchlorate off-line by ion chromatography (IC). This filter-based batch method is simple but hard to trace the perchlorate concentration that might change from moment to moment. It is essential to improve the sensitivity of the detection system so as to provide enough temporal resolution. An IC coupled mass spectrometry (IC-MS) [29–31] and IC-MS/MS [32,33] are powerful approaches for perchlorate determination, and these sensitivities grow approximately one or two orders of magnitudes compared to the IC alone. The MS is, however, costly alternative. We have tackled the improvement of the IC system without MS instrumentation. This is the first report of on-line measurement system for perchlorate in atmospheric aerosol. The monitoring results of perchlorate at Tokushima, Japan are also presented in this paper.

2. Experimental

2.1. Reagents and chromatographic system

All reagents used in this study were analytical grade, purchased from Kanto Chemical Co. Inc. or Sigma-Aldrich Co. LLC. Sartorius arium 611DI grade deionized water (>18 MΩ cm) was used throughout. An ICS 1000 ion chromatograph (Dionex Corp., all chromatographic hardware and software from this vender) was used with an IonPac AG16 (2×50 mm) guard column and an IonPac AS16 (2×250 mm) separation column along with an ASRS300 2-mm electrodialytic suppressor. Instead of a sample loop, an IonPac TAC-ULP1 (5×23 mm) anion preconcentrator column was connected to a 6-port injector. The suppressor operated at 75 mA with external water mode at a water flow rate of 1 mL/min. A 120 mmol/L NaOH eluent was used isocratically at a flow rate of 0.25 mL/min. The guard/separation columns and conductivity cell were maintained at 30 °C. Acquisition of the detector signals and system control were carried out under software control (Chromeleon Ver. 6.7).

2.2. Post-column concentrator

Post-column concentration of perchlorate was accomplished with a membrane tube based technique [34]. The current post-column concentrator was redesigned to simplify the construction as shown in Fig. 1. Before assembling the device, a Nafion membrane tube (330 μm i.d., 510 μm o.d., TT-020, Perma-Pure LLC.) was boiled in a mixture of ethanol and *N*,*N*-dimethylformamide (50% v/v) for 5 min and manually extended to be *ca.* 120%, and then washed with water. In order to convert the membrane to a H^+ form, the Nafion tube was boiled in 1 mol/L hydrochloric acid for 5 min, and washed thoroughly with water. Fifteen PEEK posts (1.57 mm dia., 25 mm long) with two 1 mm apertures each were affixed in a Diecast Aluminum enclosure (70 mm long, 100 mm wide, 28 mm tall, and 2 mm thickness, TD7-10-3, Takachi Electronics Enclosure Co. Ltd.). There were nitrogen gas inlet/outlet and four screw holes on the enclosure. The Nafion tube was cut into a 100 cm piece, and strung through the apertures of each posts as shown in Fig. 1. Both ends of the Nafion tube (*ca.* 1 mm) were inserted in a PTFE tube (0.50 mm i.d., 1.58 mm o.d., 20 mm long). With a top of Aluminum enclosure (70 mm long, 100 mm wide and 2 mm thickness) in place, four screws were put in. A column effluent flows through the tube; meanwhile, a nitrogen gas flows outside the tube to remove the solvent. As a result, involatile compounds were on-line concentrated prior to the detection. The assembled device was set in an oven (CTO-6A column oven, Shimadzu Corp.) for controlling the concentration temperature.

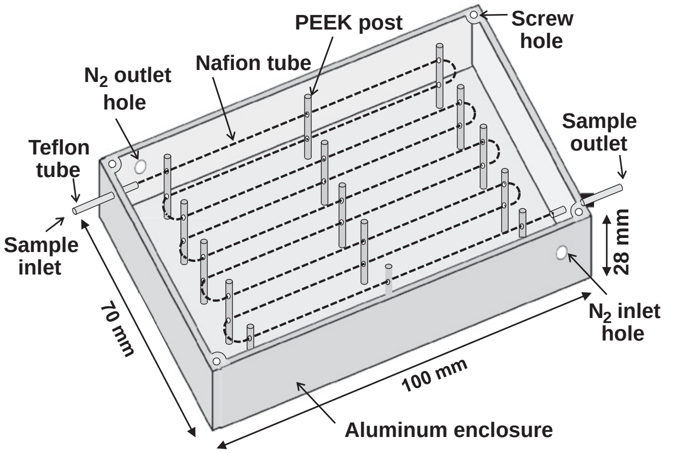

Fig. 1. Nafion tube based post-column concentrator. A top of Aluminum enclosure is not shown.

2.3. Proposed continuous analytical system

A parallel plate wet denuder (PPWD) [35,36] was used to remove gas molecules from a mixture of gases and particles in the atmospheric air. The PPWD consisted of two Plexiglas end plates and a Teflon spacer. The inner surfaces of the end plates, each with 420 mm length and 60 mm width in the active area, separated by 3 mm distance, were microstructured so as to improve the wettability with a denuder liquid. The denuder liquid was pumped to flow down each plate and was aspirated from the bottom. Air sample entered the PPWD at the bottom, and only gaseous components were removed by the denuder liquid. The particles that have passed through the PPWD were collected with a hydrophobic filter/mist chamber based particle collector (PC) [37] which sat atop the denuder. The PC consisted of an air/liquid nozzle, a cylindrical mist chamber, and an air/liquid separator. Sample airflow entered the mist chamber through a tapered Plexiglas nozzle (1.0 mm terminal orifice). The PC liquid was pumped through a stainless steel capillary (300 μm i.d., 560 μm o.d.) to the air stream just exiting the nozzle. High velocity air created a fine mist in the chamber. A hydrophobic microporous PTFE membrane filter (Fluoropore membrane filter, 0.45 μm pores, 47 mm dia., Millipore) at the top provided the airflow exit. The PC liquid mist coalesced on the hydrophobic filter surface as large droplets and fell to the bottom of the mist chamber. The particles were captured by the mist as well as at the liquid droplets/film on the filter surface. The liquid sample was aspirated from a liquid outlet aperture on the bottom of the PC.

The complete system for perchlorate measurement in the atmospheric aerosol is shown in Fig. 2. The PC can also collect water-soluble acid gases. If the acid gases enter the PC, they may act as matrix anions as discussed in the following section. The PPWD was, therefore, installed before the PC so as to remove potentially interfering acid gases. The air sample was continuously aspirated by a vacuum air pump (AP, model DOA-P501-DB, Gast manufacturing Inc.), and was controlled at 6 standard liters per minute (SLPM) with a mass flow controller (MFC1, model 8500, Kofloc Co. Ltd.). A 0.5 mmol/L hydrogen peroxide as the

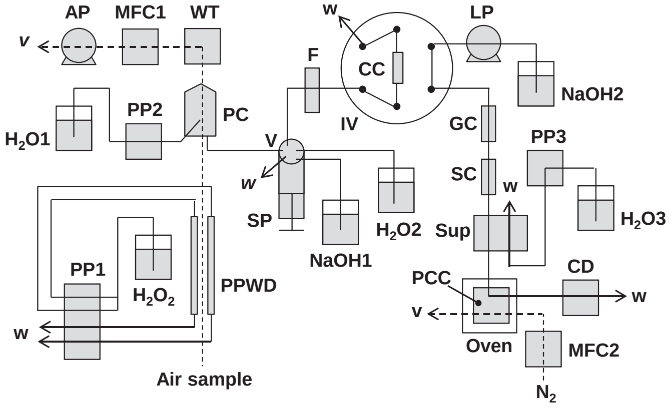

Fig. 2. Instrument schematic for continuous measurement of perchlorate in atmospheric aerosol. Key: PPWD, parallel plate wet denuder; PC, hydrophobic filter/mist chamber based particle collector; WT, water trap; MFC1 and MFC2, mass flow controller; AP, air pump; v, vent; H_2O_2, 0.5 mmol/L hydrogen peroxide as denuder liquid; PP1, PP2, and PP3, peristaltic pump; w, waste; H_2O1, water as aerosol collection liquid; V, six-way valve; SP, syringe pump; NaOH2, 10 mmol/L sodium hydroxide as matrix washing solution; H_2O2, water as column conditioning solution; F, filter; IV, six-port injection valve; CC, anion concentrator column; NaOH2, 120 mmol/L sodium hydroxide as eluent; LP, high pressure liquid pump; GC, guard column; SC, separation column; Sup, suppressor; H_2O3, water as regenerating solution; PCC, Nafion tube based post-column concentrator; N_2, nitrogen gas; CD, conductivity detector.

denuder liquid was delivered to each end plate of the PPWD at 0.25 mL/min/plate by a 4-chnannel peristaltic pump (PP1, model RP-1, Rainin Instrument Co.). The PPWD effluent was aspirated at a higher flow rate than the input flow rate to ensure that the input liquid was completely removed. The water (H_2O1) as the PC liquid was pumped into the PC chamber at 0.4 mL/min by a peristaltic pump (PP2). During air sampling, the PPWD and PC operated continuously while the PC sample was analyzed as follows. At the end of 3 h sampling cycle ($t=0$ min), the sample solution collected in the PC was aspirated through a six-way valve (V) into 10 mL capacity syringe in a syringe pump (SP, model 54022, Kloehn Co. Ltd.) at 10 mL/min. Note that the SP aspirated a 10 mL volume, regardless of the sample volume in the PC. The V was then switched and the sample solution in the syringe was pumped via a syringe filter (F, Minisart RC 25, 0.20 μm pores, Sartorius Stedim Biotech) through the anion concentration column (CC) at 2 mL/min. This sample loading procedure was repeated every 20 min until $t=160$ min. At $t=167$ min, as the washing solution for matrix ions, the 5 mL of 10 mM sodium hydroxide (NaOH1) was aspirated at 10 mL/min and delivered through the CC at 2 mL/min. The six-port injection valve (IV) was switched to an injection mode, and the remaining anions in the CC were transported to the chromatographic system equipped with the Nafion membrane tube based concentrator (PCC) operating at 80 °C concentration temperature with 10 SLPM N_2 flow rate. At $t=173$ min, the IV was switched to a load mode and the 10 mL of water (H_2O2) was aspirated at 10 mL/min and dispensed to the CC at 2 mL/min for column conditioning. At $t=180$ min, the measurement system completed this cycle and started next cycle.

3. Results and discussion

3.1. Matrix elimination

Chloride, nitrate, and sulfate are the dominant anions in atmospheric aerosol as well as other environmental samples. These ions pose a problem in the determination of trace perchlorate by IC. In particular, the broad tailing of sulfate, which elutes prior to perchlorate, covers the response of perchlorate although the perchlorate elutes much slower than the sulfate. The preconcentration-preelution technique [38,39] was examined so as to eliminate the matrix ions prior to sample injection into the ion chromatographic system. Diluted eluent (10 mmol/L NaOH, 1.0 mL/min) was used as the preeluent. In a preliminary experiment, retention times of sulfate and perchlorate for TAC-ULP1 anion preconcentrator column were measured, and the corresponding retention volumes were calculated to be 0.70 ± 0.05 and 6.07 ± 0.06 mL ($n=3$), respectively. The results suggested that a little milliliter of 10 mM NaOH preeluent could rinse the matrix from the preconcentrator column.

Next, the NaOH wash volume was optimized using water extracts from the atmospheric aerosols (PM_{10}) collected on a quartz filter (grade QM-A, 47-mm diameter, Whatman). The PM_{10} was sampled at the flow rate of 20 SLPM for 1 week. The sampling filter was ultrasonically extracted for 60 min with 30 mL of water and syringe filtered with a 0.20 μm filter. Four milliliter of the aerosol sample was loaded on the preconcentrator column followed by 1.0–7.0 mL of 10 mmol/L NaOH preeluent at 2 mL/min, and then the ions retained in the column were backflushed into the IC system. Fig. 3 shows the peak areas of perchlorate and matrix ions, mainly sulfate, as a function of the wash volume. Note that the ordinate scale for matrix peak area is three orders of magnitude larger than that for perchlorate. The matrix peak area drops dramatically at 1.0 and 4.0 mL wash, and remains at low levels in the range of 5.0–7.0 mL (18.9 ± 1.4 μS/cm min) indicating that most of the matrix have been eluted at 5.0 mL preeluent. Meanwhile, the perchlorate peak area remains nearly-constant over 1.0 mL wash volumes. The perchlorate peak areas without preeluent (0.47 μS/cm min), even at 1.0 mL (0.19 μS/cm min), are somewhat larger than others (0.11 ± 0.01 μS/cm min). Wagner et al. [40] reported the over-estimation of perchlorate in chlorinated samples with US EPA method 314.1: 1.0 mL of 10 mmol/L NaOH was used as the preeluent for a Cryptand C1 preconcentrator (Dionex Corp.) which is factory-recommended for trace perchlorate analysis in drinking water. Yamada et al. [27] also used 1.0 mL of 10 mmol/L NaOH for a TAC-LP1 anion preconcentrator (Dionex Corp.). They reported that the matrix anions led to positive interference to perchlorate determination and their undesirable effect increased with matrix concentration. The aerosol samples used in our experiments might be contained considerable matrix ions, and consequently the positive interference might appear at 1.0 mL wash volume as well as the case without preeluent. Fig. 4 shows the chromatogram of the atmospheric aerosol sample (0.34 ng/m^3 ClO_4^-) collected

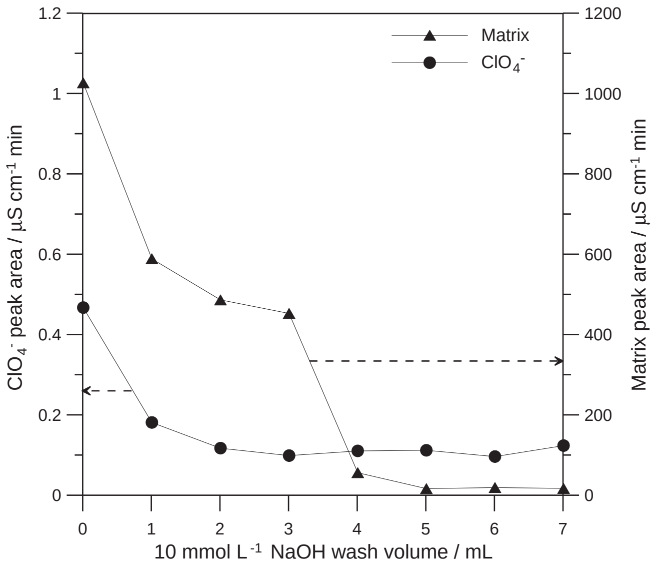

Fig. 3. Peak areas of perchlorate and matrix ions as a function of wash volume.

with filter based method (a) without preeluent, (b) with 1.0 mL, and (c) with 5.0 mL of 10 mmol/L NaOH preeluent. Chromatogram (c′) in the inset of Fig. 4 shows the output signal for 60 μg/L perchlorate spiked sample with 5.0 mL preeluent. This amounts to 8.9 ng/m^3 perchlorate in air. Clearly, chromatogram (c) is better than (a) and (b). We decided to use a 5.0 mL of NaOH as the preeluent for the subsequent experiments. For 4.0 mL loading of 1.0, 2.0, 5.0, and 10 μg/L perchlorate into the preconcentrator column, the detector response could be expressed as follows.

$$H=(0.0765\pm0.0024)C+(0.0083\pm0.0122),\quad r^2=0.9985. \tag{1}$$

$$A=(0.0404\pm0.0015)C+(0.0119\pm0.0077),\quad r^2=0.9979. \tag{2}$$

where H and A are the peak height (μS/cm) and area (μS/cm min), C is the perchlorate concentration (μg/L). The limit of detection (LOD, 3σ) and the repeatability for 10 μg/L perchlorate were 0.72 μg/L (corresponding to 2.9 ng ClO_4^-) and 4.4% ($n=3$), respectively.

3.2. Post-column concentration of perchlorate

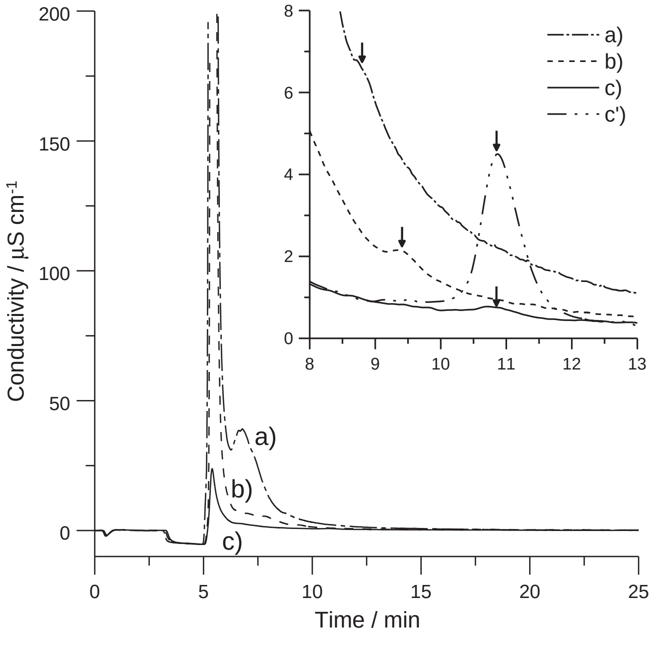

Fig. 4. Chromatograms of PM_{10} sample (a) without preeluent, (b) with 1.0 mL, (c) with 5.0 mL, and (c′) 60 μg/L perchlorate spiked with 5.0 mL of 10 mmol/L NaOH preeluent. The arrows of the inset point the perchlorate peaks.

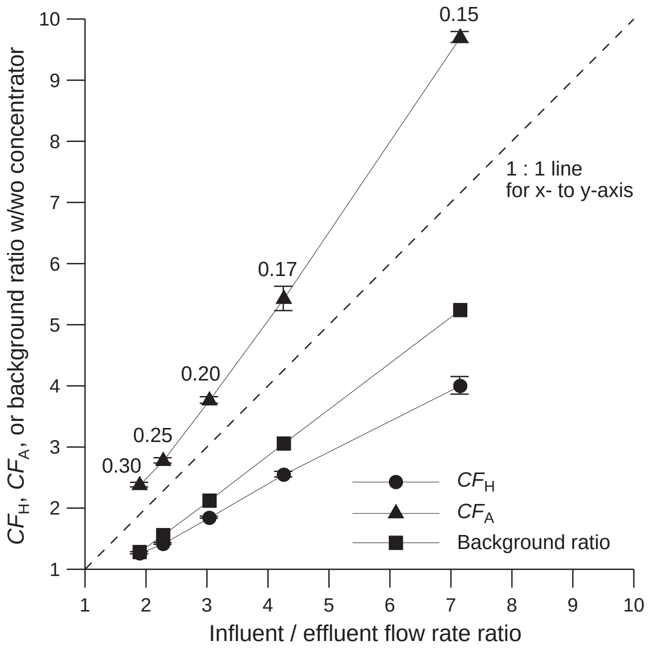

Fig. 5. CF_H, CF_A, and background conductivity ratio with/without the concentrator as a function of influent/effluent flow rate ratio.

The Nafion tube based concentrator shown in Fig. 1 was placed between the suppressor and conductivity detector and its operating parameters were characterized in terms of eluent evaporation rate, E_{eva}, calculated as difference between influent and effluent flow rate. The E_{eva} was increased dramatically with the drying nitrogen gas flow rate (3–10 SLPM) and the concentration temperature (30–60 °C). Contrary to our expectations, the E_{eva} was also increased with the eluent flow rate (0.15–0.30 mL/min). Although we did not measure the pressure drop of eluent in the concentrator, it is expected that the pressure increased with the flow rate, and thus increasing the pressure differential across the Nafion membrane enhanced the E_{eva}. Fig. 5 shows the concentration factors of perchlorate, CF, as a function of influent/effluent flow rate ratio at the influent flow rates of 0.15, 0.17, 0.20, 0.25, and 0.30 mL/min with 10 SLPM N_2 flow rate at 60 °C. The CF based on perchlorate peak height and area ratio, CF_H and CF_A, were, respectively calculated as follows.

$$CF_H=H_w/H_{wo}. \tag{3}$$

$$CF_A=A_w/A_{wo}. \tag{4}$$

where H_w and H_{wo} are the perchlorate peak height with/without concentrator, A_w and A_{wo} are the perchlorate peak area with/without concentrator. Both CF_H and CF_A are increased with the decreasing of influent flow rate due to the increase of sample residence time in the concentrator, and showed excellent linear correlation with the reciprocal of the effluent flow rate (r^2=0.9994 and 0.9985, respectively). However, the CF_H was lower than the gravimetrically measured influent/effluent flow rate ratio because of the axial dispersion, and its effect was most obvious at the lowest influent flow rate. On the other hand, the CF_A was higher than the flow rate ratio. As shown in Fig. 5, the background conductivity ratio with/without concentrator was lower than the flow rate ratio, indicating that volatile substances such as carbonic acid presented in the eluent were lost during evaporative concentration. The reduction of the background conductivity led to more sensitivity improvement than predicted by the influent/effluent flow rate ratio. Fig. 6 shows the chromatogram for 1.0 μg/L perchlorate (a) without and (b) with post-column concentrator operating at 80 °C with 0.25 mL/min sample flow rate and 10 SLPM N_2 flow rate. Note that the large peak appeared around 9 min in chromatogram b is attributed to matrix ions. The post-column concentrator is quite useful for the increase in the peak height/area of trace perchlorate. In the latter experiments, the concentrator was operated with 10 SLPM N_2 flow rate at 80 °C. For 4.0 mL analysis of 1.0, 2.0, 5.0, and 10 μg/L perchlorate with the preconcentration-preelution technique, followed by the post-column concentration approach, the detector response for peak height and area (H_{pcc} and A_{pcc}) could be expressed as follows.

$$H_{pcc}=(0.3804\pm0.0086)C+(0.0223\pm0.0469),\quad r^2=0.9992. \tag{5}$$

$$A_{pcc}=(0.3090\pm0.0089)C-(0.0208\pm0.0452),\quad r^2=0.9988. \tag{6}$$

With the post-column concentrator, the sensitivity was increased by a factor of 5.0 and 7.7 for peak height and area based calibration curves, respectively. The LOD and the repeatability for

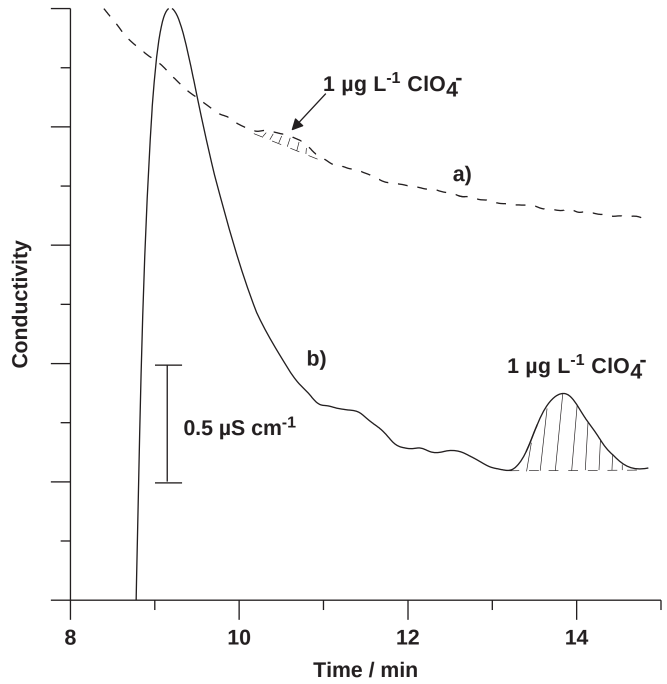

Fig. 6. Chromatograms of 1 µg/L perchlorate sample with/without the post-column concentrator.

10 µg/L perchlorate were 0.10 µg/L (corresponding to 0.38 ng ClO_4^-) and 3.6% ($n=3$), respectively.

3.3. Illustrative field data

Filed measurement of perchlorate in atmospheric aerosol using the proposed system was conducted in Tokushima, Japan (34°04′N, 134°30′E). The ambient air was aspirated from the forth-story window of the six-story building on the campus of the University of Tokushima, which abuts on a dense traffic. The entire system except the air inlet was located inside the building. A high air sampling flow rate was desirable where a significant mass of perchlorate must be collected. The PPWD permitted quantitative removal of potentially interfering soluble gases at the flow rates of up to 8 SLPM [35]. The air sampling flow rate applicable was, however, limited by the hydrophobic filter/mist chamber based PC because the PC liquid broke through the hydrophobic filter at the flow rates beyond 6 SLPM. The break-through of aerosols ranged from 0.21 to 7.8 µm mass median aerodynamic diameter was less than 0.5% at 6 SLPM [37], thus we used the flow rate of 6 SLPM for aerosol sampling. In the case of a 3 h analytical cycle at 6 SLPM (corresponding to 1.08 m^3 total sample volume), the LOD was calculated to be 0.35 ng/m^3. This value is not quite as good as recently-reported LODs of 0.013 ng/m^3 for 1 day [27] and 0.064 ng/m^3 for 1 week sampling [28]. The longer sampling duration we use, the better LOD we obtain but the lower time resolution. The proposed system was, therefore, operated with 3 h sampling cycle so as to observe circadian variation of the perchlorate concentration that could not be available from daily or weekly measurements. Fig. 7 shows the temporal variations of perchlorate concentration and ambient temperature over one and half days. The perchlorate concentration in the atmospheric aerosol ranged from below the LOD to 6.18 ng/m^3 and averaged 1.01 ng/m^3 ($n=12$). Fifty-eight percent of aerosol sample contained detectable levels of perchlorate. The perchlorate concentration changed from moment to moment within a day and increased during daytime.

In summary, we have presented an automated analysis system for perchlorate in atmospheric aerosol. Without mass spectrometric technique, the system provided the perchlorate concentration every 3 h with the LOD of 0.35 ng/m^3, and enabled us to trace the diurnal variation of perchlorate in the atmosphere.

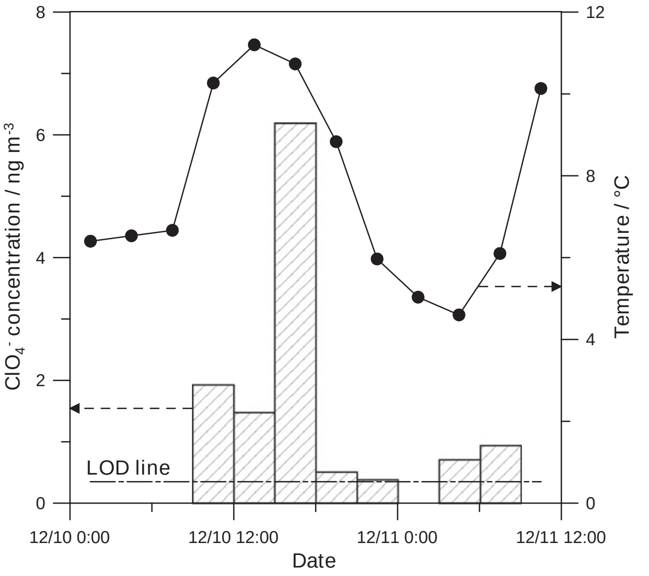

Fig. 7. Temporal variation of perchlorate in the atmospheric aerosol at Tokushima, Japan.

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