Short Communication

# Automatic monitoring system for acid rain and snow based on ion chromatography

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## Abstract

In order to investigate the mechanism of acid precipitation formation, its relationship with meteorological conditions and the source of pollutants contained in it, it was found to be much more important to know the distribution of the concentrations of various ions such as $Cl^-$, $NO_3^-$, $SO_4^{2-}$, $Na^+$, $K^+$, $NH_4^+$, $Ca^{2+}$ and $Mg^{2+}$ than its pH and electrical conductivity that used to be chiefly monitored. A reliable monitoring system for acid precipitation was developed by combining an improved pH electrical conductivity monitor and an ion chromatograph. Chemical data obtained by continuous precipitation monitoring were correlated with meteorological data.

## 1. Introduction

In the past decade, acid precipitation, which exerts an increasing influence on life on and in soil and water, has become the object of major social concern on a worldwide scale. Countermeasures to prevent its further propagation are required in order to preserve the equilibrium of ecological systems. Topics of interest concerning acid precipitation include sources of pollutants (anthropogenic, sea water, etc.), atmospheric chemistry, long-range transport of polluted air masses, scavenging and deposition of pollutants and the influence of weather on these processes. In particular, measurements of the concentrations of ions such as $Cl^-$, $NO_3^-$, $SO_4^{2-}$, $Na^+$, $K^+$, $NH_4^+$, $Ca^{2+}$ and $Mg^{2+}$ are indispensable when

studying the influence of acid precipitation on life on earth and in water [1–5].

In compliance with the above requirements, we have developed an automatic monitoring system for acid precipitation by combining an instrument to measure pH and electrical conductivity (EC) and an ion chromatograph. The system permits continuous unattended operation for 2 weeks even at sites with heavy snowfall, and allows ion chromatographic (IC) measurements even for precipitation of very low ionic content (EC below 20 $\mu$S/cm) [6–8].

## 2. Experimental

### 2.1. Apparatus and sampling

The system (Fig. 1) consists of two units, namely, a sampling system that measures pH,
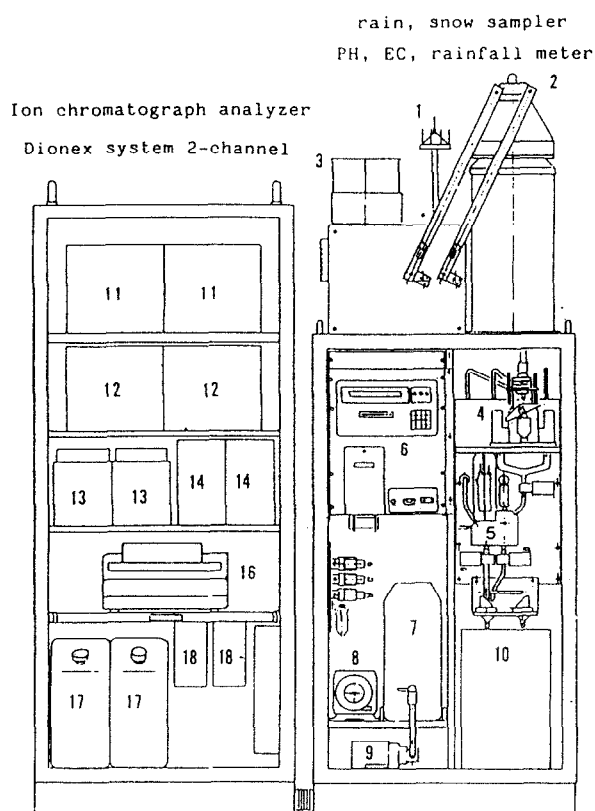
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Fig. 1. Schematic diagram of acid precipitation monitor. 1 = Rain sensor; 2 = lid; 3 = dust jar; 4 = rain gauge; 5 = cell and sensors; 6 = display printer; 7 = tank for clean water; 8 = air pump; 9 = injector pump; 10 = sampling tank; 11 = CDM-3 IC detector; 12 = eluent solution tank; 13 = DX IC pump; 14 = anion, cation column injection port; 16 = data processing unit; 17 = waste liquid tank; 18 = suppressor (ASRS, CSRS).



Fig. 2. pH meter for purified water.

EC and the amount of precipitation at intervals of 0.5 mm and an ion chromatograph capable of measuring concentrations of ions such as $Cl^-$, $NO_3^-$, $SO_4^{2-}$, $Na^+$, $K^+$, $NH_4^+$, $Ca^{2+}$ and $Mg^{2+}$ per 1 mm of precipitation.

By adoption of a glass electrode of the flow-through type for purified water, shown in Fig. 2, this system permits pH measurements even at EC lower than 20 $\mu$S/cm.

The ion chromatograph used was either from Dionex or from Yokogawa Analytical Systems, both of which have two-channel systems allowing the simultaneous determination of cations and anions. They are equipped with a suppressor to decrease the background conductivity of the
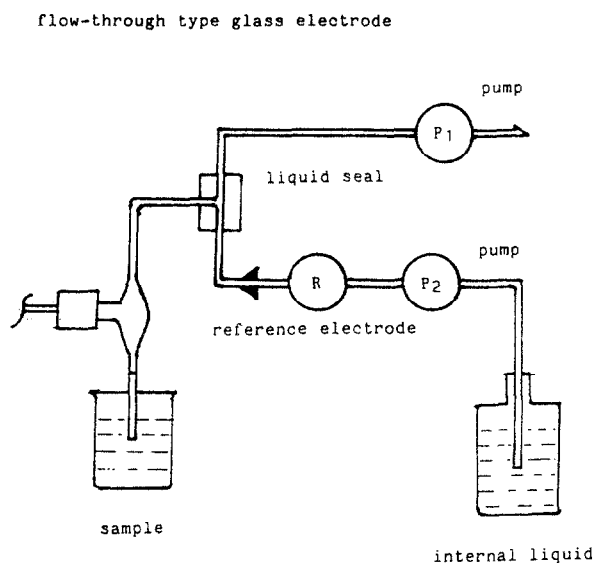
eluent solution, ensuring measurements of high sensitivity and accuracy for low ionic concentrations.

The Dionex unit, having a membrane suppressor assembled with an electrode, does not need additional liquid as it has a regenerating system for eluent solution discharged form the detector. The Yokogawa unit contains a micromembrane suppressor. As soon as the detector of this monitoring system detects precipitation, its pump starts and, after 35 min, standard liquid (a mixture of several kinds of ions) is automatically fed into the system and analysed to produce calibration diagram. Subsequently, automatic analysis of rainfall sampled by the pump is conducted in real time as shown in the time chart in Fig. 3.

When precipitation is detected by the rain sensor (1), the cover of the precipitation collector (2) is opened and moves to the dust jar (3). The amount of precipitation is measured by a rain gauge (4) and pH, EC and temperature are measured (5). Part of the precipitated water is injected into the ion chromatograph through a filter.

In the Dionex system, a pump (DX100), detector (CDM-3), column, self-regenerating suppressors for anions (ASRS) and for cations (CSRS) in two channels are installed for the
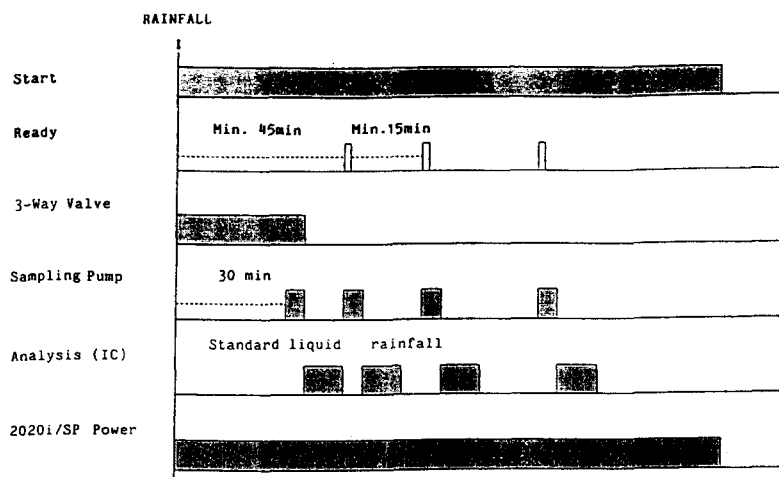
Fig. 3. Automatic ion analyser for acid rain (time chart).

simultaneous measurement of anions and cations.

Data on precipitation analysis processed by the chromatogram processor are printed and then stored on floppy disk via a recording unit (6).

## 2.2. Reagents

The eluent was prepared from of high-purity grade $Na_2CO_3$, $NaHCO_3$ and methanesulphonic acid (Waco Junyaku) and distilled water.

Stock standard solutions of the various ions (each 1000 mg/l) were prepared from NaCl, $NaNO_3$, $Na_2SO_4$, $(NH_4)_2SO_4$, KCl, $Mg(NO_3)_2 \cdot 6H_2O$ and $CaCl_2 \cdot 2H_2O$ of high-purity grade (Waco Junyaku) and distilled water. From these stock standard solutions, mixed working standard solutions including all of the above ions were prepared.

## 3. Results and discussion

### 3.1. Analytical conditions

Conditions for the determination of anions and cations using the ion chromatograph are given in Table 1.

Examples of anion and cation separations of

snow conducted by means of the Dionex system are shown in Fig. 4a and b, respectively.

### 3.2. Preparation of artificial rainwater

Artificial rainwater with ion concentrations equal to the annual mean concentrations found in Japan was prepared [9]: chloride 1.60, nitrate 1.10, sulphate 4.80, sodium 1.00, ammonium 0.55, potassium 0.10, magnesium 0.20 and calcium 0.80 $\mu$g/ml (pH 4.7).

### 3.3. Reproducibility test by using artificial rainwater

Tests of the system on a 24-h basis making use of artificial rainfall of 1 mm/h were repeatedly carried out for 20 days to evaluate the reproducibility of the measurement and performance of the system on a long-term basis. During that period, stable measurement was verified without any malfunction of the system. Owing to the adoption of the Dionex ion chromatograph equipped with both ASRS and CSRS, which does not require the supply of regenerated solution, the system was operated free from maintenance throughout that period.

The results are given in Table 2. The relative standard deviations (R.S.D.) for ions such as chloride, nitrate, sulphate, sodium, magnesium and calcium appear very reasonable (2–3%), but

Table 1
Analytical conditions for Dionex ion chromatograph for the measurement of anions and cations

|  | Anions | Cations |
| --- | --- | --- |
| Model | Dionex DX100 | Dionex DX100 |
| Detector | Dionex CDM-3 | Dionex CDM-3 |
| Guard column | 50 × 4 mm I.D. Ion Pac AG4A-SC | 50 × 4 mm I.D. Ion Pac CG12 |
| Separation column | 250 × 4 mm I.D. Ion Pac AS4A-SC | 250 × 4 mm I.D. Ion Pac CS12 |
| Eluent | 1.8 m$M$ Na$_2$CO$_3$–1.7 m$M$ NaHCO$_3$ | 20 m$M$ CH$_3$SO$_3$H |
| Flow-rate of eluent | 1.7 ml/min | 1.1 ml/min |
| Sample volume | 50 $\mu$l | 50 $\mu$l |
| Suppressor | ASRS[a] | CSRS[b] |

[a] ASRS = anion self-regenerating suppressor for recycling eluent solution after flowing through the detector.
[b] CSRS = cation self-regenerating suppressor for recycling eluent solution after flowing through the detector.
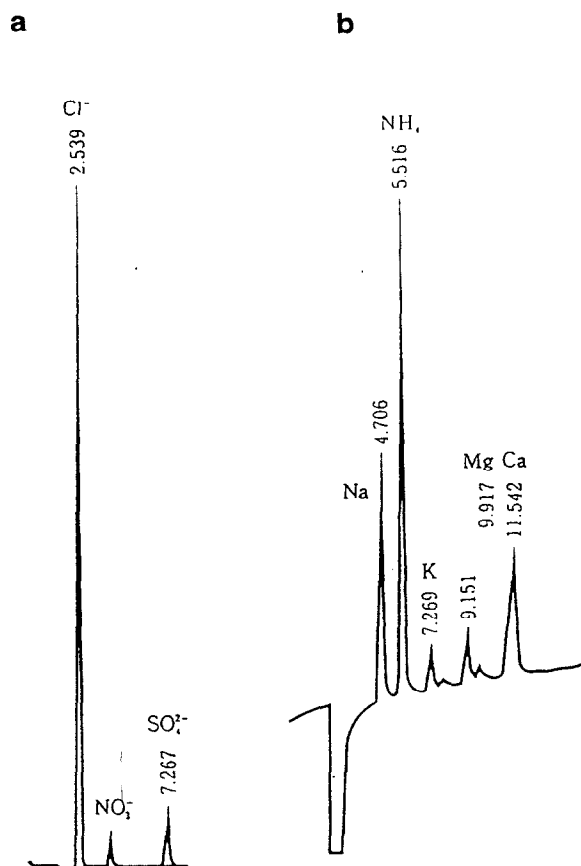


Fig. 4. Examples of (a) anion and (b) cation separations in snow. Numbers at peaks are retention times in min.

those for ammonium (4.6%) and potassium (8.7%) are poor, probably because of the difficulty in separating the two adjacent peaks of these components in the chromatogram. In the context of field measurements, this degree of variation for ammonium and potassium can be accepted.

### 3.4. Limit of sensitivity

As shown in Table 3, reasonable detection limits at a signal-to-noise ratio of 3 are obtained.

The data suggest direct field measurements of these chemicals at low concentrations can be feasible without any preliminary treatment of the sample or the use of a condensation column.

### 4. Conclusions

Until recently, monitoring of acid precipitation has been limited to measurements of pH, EC and quantity of rainfall. Therefore, there were insufficient data available to investigate quickly the mechanism of its generation or to locate the origin of its components, although time-consuming analysis by sending rainwater accumulated in storage tanks for 1–2 weeks to a remote laboratory having ion chromatographs has been possible.

Table 2
Results of reproducibility of a running test using an artificially prepared rainwater sample (24 h) $n = 31$

| Ion | Content (mg/l) | Minimum (mg/l) | Maximum (mg/l) | Mean (mg/l) | R.S.D. (%) |
|-----|-----|-----|-----|-----|-----|
| Chloride | 1.6 | 1.44 | 1.65 | 1.58 | 2.5 |
| Nitrate | 1.10 | 1.05 | 1.18 | 1.10 | 3.4 |
| Sulphate | 4.80 | 4.31 | 5.10 | 4.85 | 3.0 |
| Sodium | 1.00 | 0.99 | 1.09 | 1.07 | 2.2 |
| Ammonium | 0.55 | 0.54 | 0.06 | 0.57 | 4.6 |
| Potassium | 0.10 | 0.09 | 0.12 | 0.10 | 8.7 |
| Magnesium | 0.20 | 0.19 | 0.22 | 0.20 | 2.5 |
| Calcium | 0.80 | 0.76 | 0.86 | 0.82 | 2.7 |

With the present system, combining an automatic sampling unit and an ion chromatograph, enabling real-time measurement of various ions in addition to pH, EC, etc., reliable monitoring of variations in ion concentrations with time or changes in barometric pressure and wind direction is feasible, thus ensuring very accurate analysis of the generation of acid precipitation and correlations with its source and weather conditions in the future.

Table 3
Detection limits for ions in rainwater (signal-to-noise ratio = 3)

| Ion | Detection limit ($\mu$g/l) | Ion | Detection limit ($\mu$g/l) |
|-----|-----|-----|-----|
| Chloride | 5 | Sodium | 5 |
| Nitrate | 10 | Ammonium | 10 |
| Bromide | 15 | Potassium | 10 |
| Sulphate | 25 | Magnesium | 5 |
|  |  | Calcium | 10 |

## 5. Acknowledgements

## 6. References

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