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# Determination of anions at the ng/l level by means of switching valves to eliminate the water-dip interference

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## Abstract

It is well known that anions, such as chloride, nitrate and sulphate can be determined relatively easily at the  $\mu\text{g/l}$  level using an on-line concentrator column. In recent years, however, ultra-pure water containing only ng/l levels of anions or cations is demanded by the most advanced semiconductor factories or power generation plants. For the determination of anions and cations at the ng/l level in such ultra-pure water, higher sensitivity is required. To achieve this, it is necessary to eliminate the water-dip which interferes with the determination of chloride at the ng/l level. We developed and tested a water-dip cutting system consisting of switching valves and a water-dip cutting column. When we combined this with an on-line concentration system, we were able to determine chloride, nitrite, bromide, nitrate, phosphate and sulphate at the ng/l level.

## 1. Introduction

Ion chromatography (IC) is a popular method for ion analysis (especially anions) for several reasons. First, many anions can be determined quickly with high precision. Second, since IC is a chromatographic technique, many anions or cations can be determined simultaneously, and different chemical species of same element (*e.g.* chlorite, chlorate and chloride) can be separated. Third, low level ion analysis can be done relatively easily [1–5]. This third feature is important for semiconductor factories and power generation plants that use ultra-pure water in manufacturing process and heat transfer systems [6].

In recent years, these industries have demanded even purer water, allowing only ng/l levels of anions and cations. There are two approaches to achieve the levels of sensitivity required. The first is to improve the signal-to-

noise ( $S/N$ ) ratio, and the second is the use of an on-line concentration column, which increases the amount of ions introduced into the separation column, a widely used technique for  $\mu\text{g/l}$ -level ion analysis [1–3]. Unfortunately, both techniques are sometimes insufficient to determine ng/l-level anions, because the large negative water peak (water-dip) interferes with the determination of ng/l levels of fluoride and chloride. Since ng/l levels of chloride are especially important in semiconductor factories and power-generation plants, the development of a method to avoid water-dip interference is particularly significant. Some methods for avoiding water-dip interference have been already reported [7–9], but they are not satisfactory for the determination of ng/l-level chloride or polyvalent anions, such as phosphate or sulphate.

This paper describes the development of a new method for avoiding water-dip interference to determine ng/l-level chloride and other anions eluted after chloride. The method uses a system

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consisting of a water-dip cutting column and two column-switching valves. Using this system coupled with the well-known on-line concentration technique, ng/l levels of chloride were determined.

## 2. Experimental

### 2.1. Instrumentation

A Model IC7000 ion chromatographic analyzer (Yokogawa Analytical Systems, Tokyo, Japan) with a conductivity detector and automatic switching high-pressure six-port valves was used in all experiments. A Model WS 7000 data station (Yokogawa Analytical Systems) was used for data acquisition. The columns used were an Excelpak ICS-A44 (polystyrene based, 150 mm × 4.9 mm I.D.) as a separation column, and an Excelpak ICS-ANC (polyvinyl alcohol based, 20 mm × 4.6 mm I.D.) as an on-line concentration column. The water-dip cutting column (75 mm × 4.9 mm I.D.) was packed with the same anion-exchange resin as the Excelpak ICS-A44. HPS-SA1, which was made from Nafion tube, was used as a suppressor. The separation column, the cutting column and the suppressor were kept at 40°C. The eluent and the regenerator were degassed by an on-line vacuum degassing unit. All columns and the suppressor were manufactured by Yokogawa Analytical Systems.

### 2.2. Reagents

Sodium carbonate (Japan Industrial Standards primary standard-grade, Asahi Glass, Tokyo,

Japan) was used for preparing the eluent, and sulphuric acid (reagent-grade, Wako Pure Chemicals, Osaka, Japan) was used to regenerate the suppressor. Highly purified sodium carbonate is necessary for determining ng/l levels of anions, because inorganic contaminants interfere with the determination of samples. For example, when a sample contains a smaller amount of chloride than the eluent, a negative peak appears at the same retention time as chloride.

Standard stock solutions of chloride, nitrite, bromide, nitrate, and sulphate were prepared by dissolving appropriate amounts of sodium salts (IC grade, Kanto Chemical, Tokyo, Japan) in water. Samples were prepared by diluting stock solutions with purified water. Water used in the analysis was purified with a Millipore (Bedford, MA, USA) Milli-Q water purification system.

All samples and the eluent were prepared in aged vessels made of polyethylene or polypropylene. The Vessels were aged by soaking them in ultra-pure water for 3 days, and replacing ultra-pure water every day.

### 2.3. Eluent and regenerator

The eluent, 4.0 mM Na<sub>2</sub>CO<sub>3</sub>-4.0 mM NaHCO<sub>3</sub>, was prepared daily and filtered before use. The flow-rate was 1.0 ml/min. The regenerator 15 mM H<sub>2</sub>SO<sub>4</sub>, was used at a flow-rate of 1.0 ml/min.

### 2.4. Procedure

The sample was passed by the sampling pump into the concentration column, where anions were concentrated. During this step, the posi-

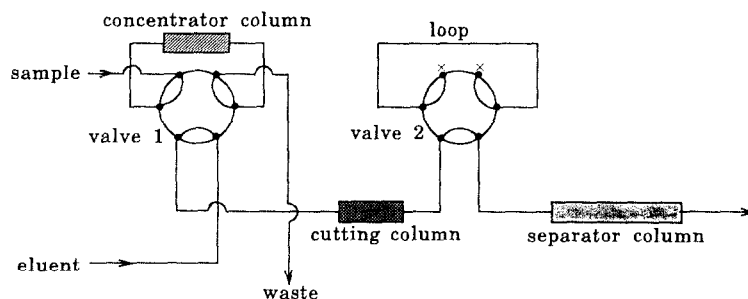


Fig. 1. Sample concentration and water-dip cutting procedure: concentration of sample on the concentration column.

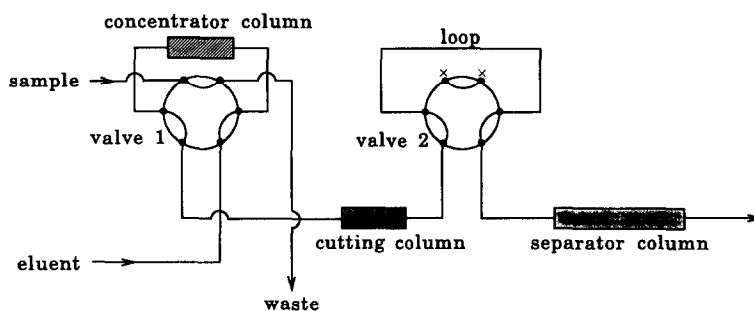


Fig. 2. Sample concentration and water-dip cutting procedure: the water-dip cutting process. Separation of chloride and other anions from water and early-eluting anions.

tions of valve 1 and valve 2 were as shown in Fig. 1.

After a concentration period of normally 5–20 min, the positions of valve 1 and valve 2 were changed, as in Fig. 2. The eluent flowed through the concentration column, and anions were eluted from this column to the cutting column. On the cutting column, water and anions eluting before chloride were separated from chloride and anions eluting after chloride.

Water and the early-eluting anions were carried to the loop, and the position of valve 2 was then changed as in Fig. 3 (normally 1.5 min after the switching of valves 1 and 2 in Fig. 2). Then chloride and the anions eluting after chloride were carried to the separation column. On this column, chloride and the other anions were separated from each other, and detected by the conductivity detector. After this determination, positions of valve 1 and valve 2 were changed as in Fig. 2, and the water and early-eluting anions

were carried to separation column from the loop and discharged.

### 3. Results and discussion

#### 3.1. Effects of the water-dip cutting column

A typical chromatogram of anions obtained using a common on-line concentration system is shown in Fig. 4. This shows that the water-dip clearly interferes with the determination of chloride and nitrite. The volume of the water-dip depends on the volume of the sample introduced into the separation column. The most effective way of reducing the volume of the water-dip is to reduce the volume of the concentration column. There is a limit to this, however, because it reduces the loading capacity of the concentration column. Increasing the sample volume increases the peak signal, but, because the volume of the water-dip does not change, the quantifiability of

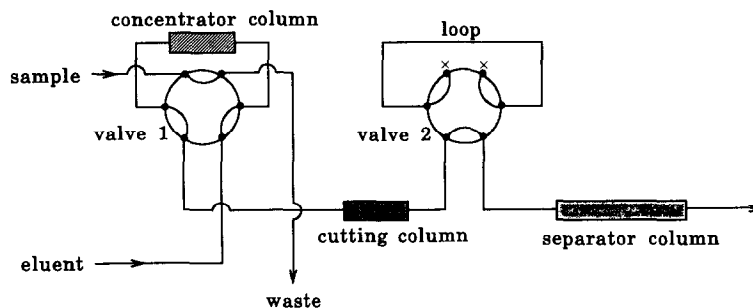


Fig. 3. Sample concentration and water-dip cutting procedure: determination of chloride and anions eluted after chloride.

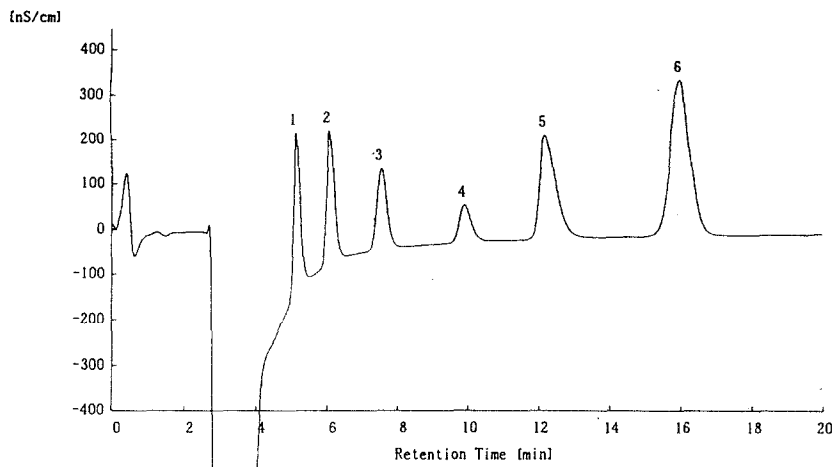


Fig. 4. Chromatogram of low-level anions obtained using an on-line concentration method. Analytical conditions were as in Experimental. The concentration time was 10 min at a sample flow-rate of 2.0 ml/min. Peaks: 1 = chloride ( $0.5 \mu\text{g/l}$ ); 2 = nitrite ( $0.75 \mu\text{g/l}$ ); 3 = phosphate ( $1.5 \mu\text{g/l}$ ); 4 = bromide ( $0.5 \mu\text{g/l}$ ); 5 = nitrate ( $1.5 \mu\text{g/l}$ ); 6 = sulphate ( $2.0 \mu\text{g/l}$ ).

chloride is not improved. In addition, a very long pre-concentration time is required. Using a separation column with a large ion-exchange capacity, or controlling the anion retention time by adding a modifier to the eluent, will separate chloride from the water-dip, but these changes would result in such a long analysis time that phosphate would not elute [5]. It follows, therefore, that the most effective way to remove the

water-dip is to prevent the introduction of water into the separation column.

A chromatogram obtained using the water-dip cutting column and the on-line concentration column is shown in Fig. 5. The sample was as same as in Fig. 4. In this system (see Figs. 1–3), water and fluoride are separated in the cutting column from chloride and the anions eluting after it. After this cutting step, chloride and the

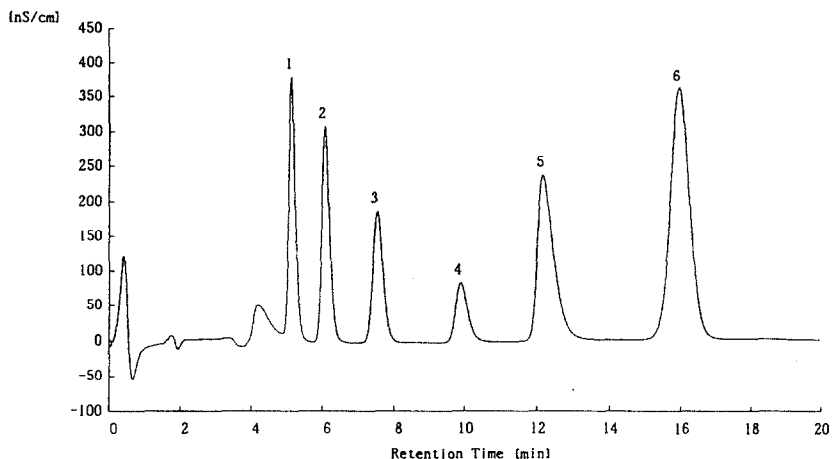


Fig. 5. Chromatogram of low-level anions obtained using the water-dip cutting system and on-line concentration method. The analytical conditions were the same as for Fig. 4, with the addition of the water-dip cutting column. Peaks: 1 = chloride; 2 = nitrite; 3 = phosphate; 4 = bromide; 5 = nitrate; 6 = sulphate; the concentrations of all the ions were same as in Fig. 4.

anions eluting after it are carried to the separation column.

When using a concentration column with a large volume (producing a large water-dip), adjustment of the cutting time (valve-switching time) is all that is required to eliminate the water-dip.

### 3.2. Sampling and sample preparation

Sampling and sample preparation techniques are important when determining anions at the ng/l level, because contamination at the  $\mu\text{g/l}$  level may frequently occur from the atmosphere [1] and the measurement system. Contamination from the system can be prevented by using pumps equipped with a self-washing mechanism, which automatically washes the plunger and plunger seal with ultra-pure water. On the other hand, preventing contamination from the atmosphere is very difficult. On-line sampling is the best solution for this problem, but on-line preparation of calibration samples is not easy. It is necessary, though, to use samples immediately after preparation to minimize the contamination from the atmosphere.

Another important consideration when preparing calibration samples is how to prepare the zero concentration sample. Very small amounts of contamination from water is unavoidable, thus a zero concentration sample cannot be prepared, but this contamination is serious problem when determining anions at the ng/l level. Therefore, water for ng/l-level anion analysis must be contaminant certified. External contamination for the "blank" was minimized by direct connection of a Milli-Q water purification system to the pre-concentration sampling pump.

Good linearity was obtained for chloride (0.1–1.0  $\mu\text{g/l}$ ) and sulphate (0.1–1.0  $\mu\text{g/l}$ ) using calibration samples prepared as described above. The  $R^2$  value of the calibration curves were 0.998 (chloride, peak height) and 0.992 (sulphate, peak height). Under the conditions of Fig. 5, the detection limit for chloride was 2 ng/l at a signal-to-noise ratio of 3.

The coefficients of variation for 0.5  $\mu\text{g/l}$  of chloride was 1.2% (peak area) and 0.8% (peak

height); those for 1  $\mu\text{g/l}$  of sulphate were 1.0% (peak area) and 0.7% (peak height). Thus this system can be regarded as having good reproducibility.

### 3.3. Life of the cutting column

In this system, water is separated from chloride by the cutting column, which is packed with anion-exchange resin. Thus, if the anion-exchange capacity changes within a short period, it is necessary to change the time-sequence programme of the switching-valve positions. This becomes a problem for continuous measurement in industrial applications. However, because the samples and the eluent contain very low levels of anions, the reduction of the anion-exchange capacity of the cutting column was negligible. The cutting column could be used for a minimum of three months without any significant deterioration.

### 3.4. Determination of anions in some actual samples

The chromatogram of anions in the recycling water of a boiler system in a thermal power (Fig. 6) shows that ng/l levels of chloride, nitrite, nitrate and sulphate were detected. The large negative peak that appeared just before chloride was due to ammonium hydroxide, an additive in recycling water. In this case, chloride could not be determined without a water-dip cutting system.

Fig. 7 is a chromatogram of a semiconductor water rinse. In this chromatogram, the concentration of nitrite was relatively high. It is speculated that this is due to atmospheric contamination during the rinse process. Nitrite is a typical air contaminant. Because nitrite increases directly with increasing exposure of the sample to air, the sampling method is of importance when determining low levels of nitrite.

Fig. 8 shows a chromatogram of anions in the washing water of the inner surface of pipes for an ultra-pure water delivery system. By measuring chloride and several anions at the ng/l level, it is possible to estimate the cleanliness of the

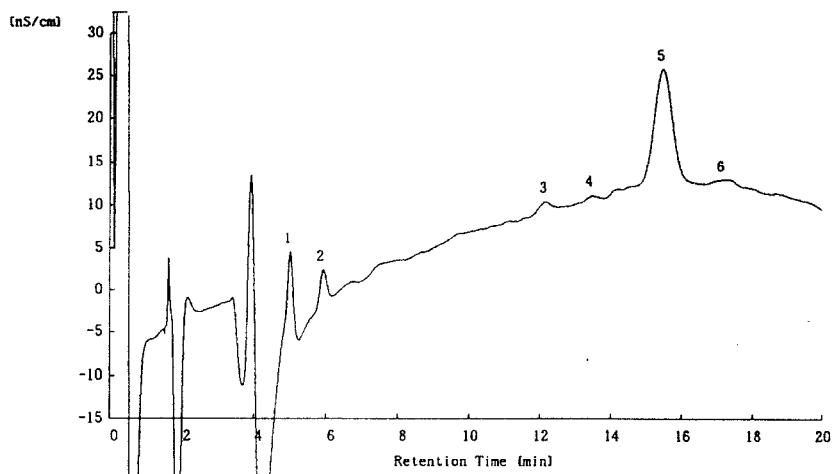


Fig. 6. Chromatogram of anions in the recycling water of the boiler system in a thermal power-generation plant. The analytical conditions were the same as for Fig. 5. Peaks: 1 = chloride (70 ng/l); 2 = nitrite (30 ng/l); 3 = nitrate (20 ng/l); 4 = unknown; 5 = sulphate (25 ng/l); 6 = unknown.

pipes. Chloride, nitrite, phosphate, bromide, nitrate and sulphate were determined at the sub- $\mu\text{g/l}$  or  $\text{ng/l}$  level. By controlling the anion elution time, it is possible to separate chloride from the water-dip, but then sulphate or phosphate take a long time to elute or are not eluted

at all. However, by using this water-dip cutting system, monovalent anions and polyvalent anions, such as sulphate or phosphate, can be determined simultaneously.

Fig. 9 shows the measurement of anions in  $\text{CO}_2$  gas used in the electronics industry. The

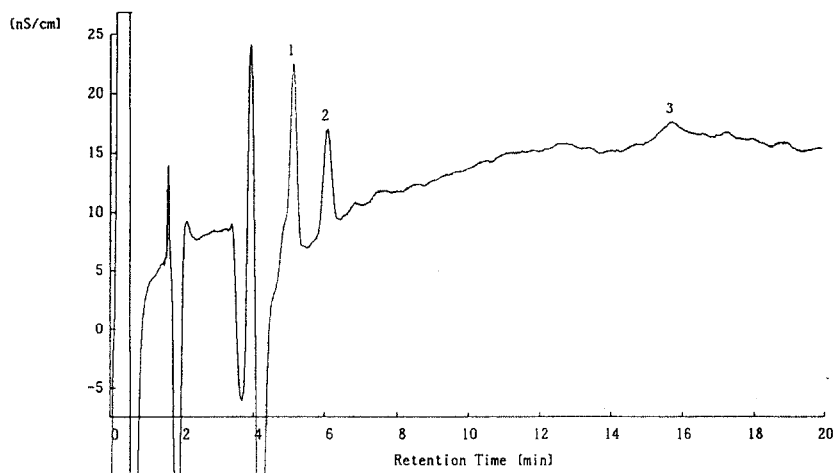


Fig. 7. chromatogram of the anions in the washing water of a semiconductor. The analytical conditions were the same as for Fig. 5. Peaks: 1 = chloride (16 ng/l); 2 = nitrite (22 ng/l); 3 = sulphate (8 ng/l).

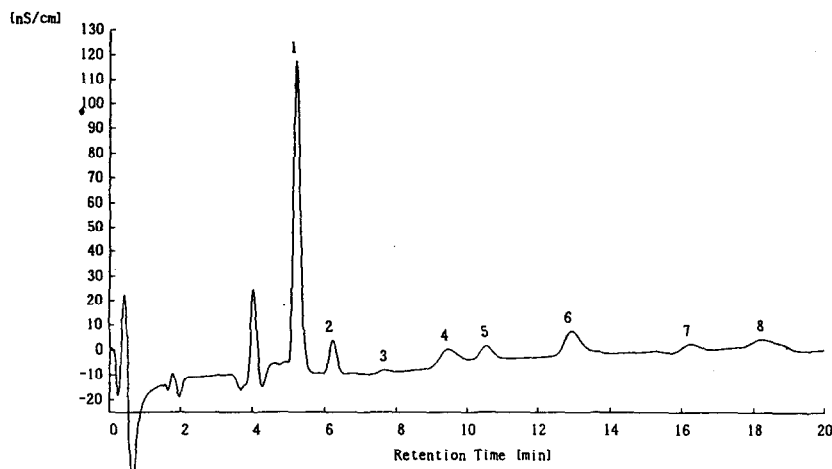


Fig. 8. Chromatogram of anions in the rinsing water of the inner surface of a stainless steel pipe. The analytical conditions were the same as for Fig. 5. Peaks: 1 = chloride (150 ng/l); 2 = nitrite (30 ng/l); 3 = phosphate (10 ng/l); 4 = unknown; 5 = bromide (50 ng/l); 6 = nitrate (50 ng/l); 7 = sulphate (10 ng/l); 8 = unknown.

sample was prepared by bubbling  $\text{CO}_2$  into ultra-pure water, therefore very large amounts of carbonate and hydrogen carbonate are found in this sample. These ions interfere with the determination of chloride, in the same way as

water. The water-dip cutting system can be used to prevent the interference of carbonate and bicarbonate. This example shows that the water-dip cutting system is also useful for avoiding the influence of sample matrixes.

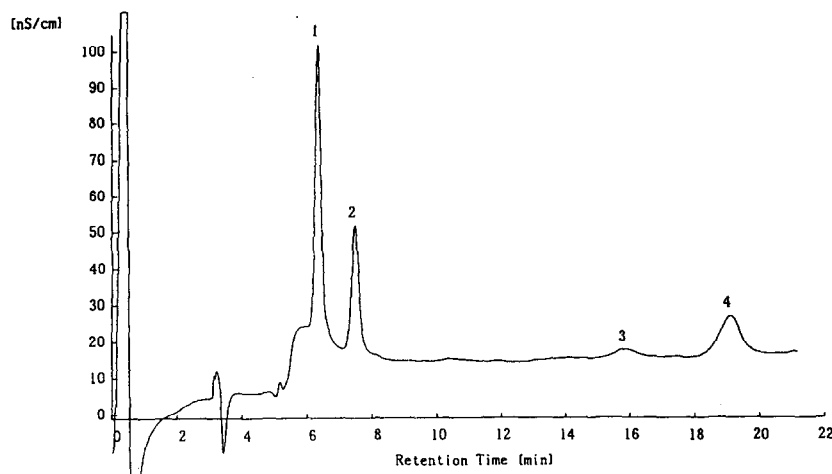


Fig. 9. Chromatogram of the anions in  $\text{CO}_2$  gas. The analytical conditions were the same as for Fig. 5. The sample was prepared by bubbling  $\text{CO}_2$  into ultra-pure water. Peaks: 1 = chloride (240 ng/l); 2 = nitrite (180 ng/l); 3 = nitrate (50 ng/l); 4 = sulphate (150 ng/l).

#### 4. Conclusions

Using a water-dip cutting column and an on-line concentration column, connected by automatic-switching valves, chloride and the anions eluting it were determined at the ng/l level with good precision. This system was useful for determining chloride and the anions eluting after it in ultra-pure water, such as that used in semiconductor factories or power-generation plants. This system is also useful for eliminating the influence of sample matrixes.

#### 5. References

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