

Short communication

Ultra-pure water for ion chromatography

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Abstract

Water with ionic concentrations substantially below 1 $\mu\text{g/l}$ is an increasing requirement for high sensitivity ion chromatographic analysis. The resistivity of the water is not an adequate guide to impurity levels at less than 1 $\mu\text{g/l}$ due to the practical limitations in resistivity measurement and to the non-linear variation of resistivity with impurity ion concentration. A water purification system is described using inter-stage monitoring to overcome these limitations and to ensure ultra-trace ionic levels. Some examples of cation analyses are included.

Keywords: Inorganic anions; Inorganic cations; Water, ultra-pure

1. Introduction

State-of-the-art ion chromatographs offer very high sensitivity for the detection and determination of ions. With preconcentration, limits of detection are at low ng/l levels and are mainly limited by contamination.

Ultra-pure water of guaranteed purity is required to make good use of this sensitivity.

Water of sufficient purity from a laboratory water purifier cannot be guaranteed by on-line resistivity monitoring due to the limitations of resistivity as a measure of water purity.

A system designed specifically to achieve real confidence in water purity is described.

2. Limitations of resistivity

At impurity concentrations below 1 $\mu\text{g/l}$ resistivity is not an adequate indication of the ionic content of ultra-pure water.

On-line resistivity monitors are accurate, at best, to $\pm 0.1 \text{ M}\Omega \text{ cm}$, more typically to $\pm 0.2 \text{ M}\Omega \text{ cm}$.

They are very dependant on accurate temperature measurement and on freedom from contamination [1].

In ultra-pure water the ionic impurities present are those which remain from the feedwater and those acquired during water treatment. The most common impurity inorganic ions are sodium, calcium, ammonium, chloride, nitrate and sulphate. During the deionisation process the anions and cations are removed separately, therefore, there is often a preponderance of one type of impurity ion over the others [2]. The overall charge is balanced by a change in the dissociation balance of the water.

The resistivity is the reciprocal of the conductivity. The conductivity, $C \mu\text{S/cm}$, is given by the sum of the contributions of the individual ions.

$$C = \text{SUM} \frac{(IC \times EC)}{(EW)} \times 10^{-3}$$

where IC = ion concentration in $\mu\text{g/l}$; EC = equivalent conductance of ion in $\text{cm}^2/\Omega \text{ equiv.}$; EW = equivalent mass in g.

The conductivity is made up of contributions from the impurity ions and from hydrogen and hydroxyl

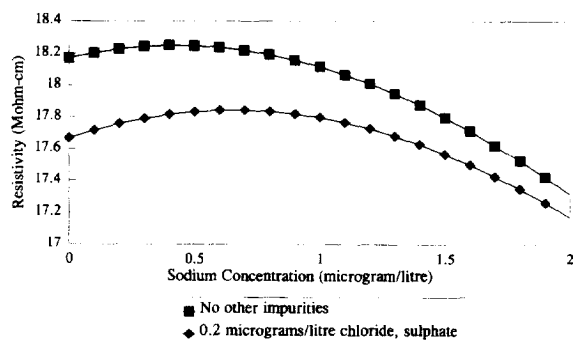


Fig. 1. Effect of sodium on resistivity; calculated values.

ions. The concentrations are governed by two relationships.

$$[\text{Anions}] + [\text{OH}^-] = [\text{Cations}] + [\text{H}^+]$$

and

$$[\text{H}^+] \times [\text{OH}^-] = 1.012 \cdot 10^{-14} \text{ (at } 25^\circ\text{C)}$$

where [] = ionic concentration in equiv./l.

The equivalent conductance of H^+ is $349.8 \text{ cm}^2/\Omega \text{ equiv.}$, far higher than all other ions (which typically have conductances of 40 to 75). As impurity cation concentrations increase the concentration of hydrogen ions decrease. This effect can outweigh the added conductivity and cause the resistivity to rise with increasing impurity concentrations. This is illustrated in Fig. 1 which shows the variation of resistivity with sodium concentration in the presence and absence of chloride and sulphate ions. The resistivity rises above that of absolutely pure water before starting to decrease. The agreement between the calculated and experimental values is described

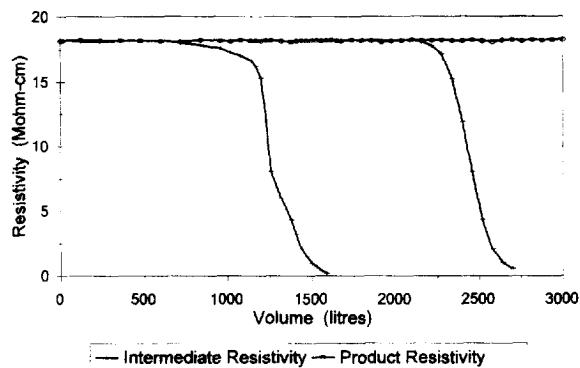


Fig. 2. Intermediate and final water qualities.

in Pate [2]. The calculations are described in more detail in Whitehead [3].

Table 1 gives some examples of the concentrations of individual ions which it is calculated could be present in water of various resistivities, using the above procedure.

Practical factors and the nature of the resistivity of ultra-pure water limit the value of resistivity monitoring for sub- $\mu\text{g/l}$ ionic concentrations.

3. Guaranteed water purity

Mixed premium-grade ion-exchange resins will remove virtually all ionic impurities from the water as long as the resins are not starting to exhaust. To be sure that trace ions are not appearing undetected in the product water the resistivity must be measured before the final polishing resin.

In the Maxima laboratory water purification system, pretreated water is pumped through a purification cartridge containing organic absorbent and

Table 1

Calculated concentration of individual ions which could be present in water of various resistivities

Ions	Concentration in $\mu\text{g/l}$ at resistivity of			
	18.2 $\text{M}\Omega \text{ cm}$	18.0 $\text{M}\Omega \text{ cm}$	17.5 $\text{M}\Omega \text{ cm}$	15.0 $\text{M}\Omega \text{ cm}$
Na^+	0.8	1.3	1.8	3.6
Cl^-	<0.1	0.15	0.5	2.1
Fe^{2+}	2.0	2.4	3.0	5.4
$\text{Na}^+ + \text{Cl}^- + \text{SO}_4^{2-}$ ^a	<0.1	0.3	1.1	5.4
$\text{Na}^+ + \text{Cl}^-$ (as NaCl)	<0.1	0.2	0.9	5.0

^a Equal concentrations.

Table 2
Calibration data

Ion	Counts/($\mu\text{g/l}$)	Correlation coefficient
Na^+	106.8	0.9995
NH_4^+	53.9	0.9724
K^+	60.6	0.9956
Mg^{2+}	172.4	0.9981
Ca^{2+}	111.3	0.9973

highly regenerated Hypex ion-exchange resins, through a resistivity cell and then through a second identical cartridge before final filtration and UV disinfection.

The first resistivity cell monitors the exhaustion of the first cartridge. When the resistivity has fallen to $1 \text{ M}\Omega \text{ cm}$ the first cartridge is replaced. During this

Table 3
Results on ultra-pure water samples

Sample	Na^+ (ng/l)	NH_4^+ (ng/l)	K^+ (ng/l)	Mg^{2+} (ng/l)	Ca^{2+} (ng/l)
b	4	105	15	<6	<10
c	3	65	9	<6	<10
d	4	30	<5	<6	<10

b=Maxima product water (day 1).

c=Maxima product water (day 2)

d=Maxima cartridge water.

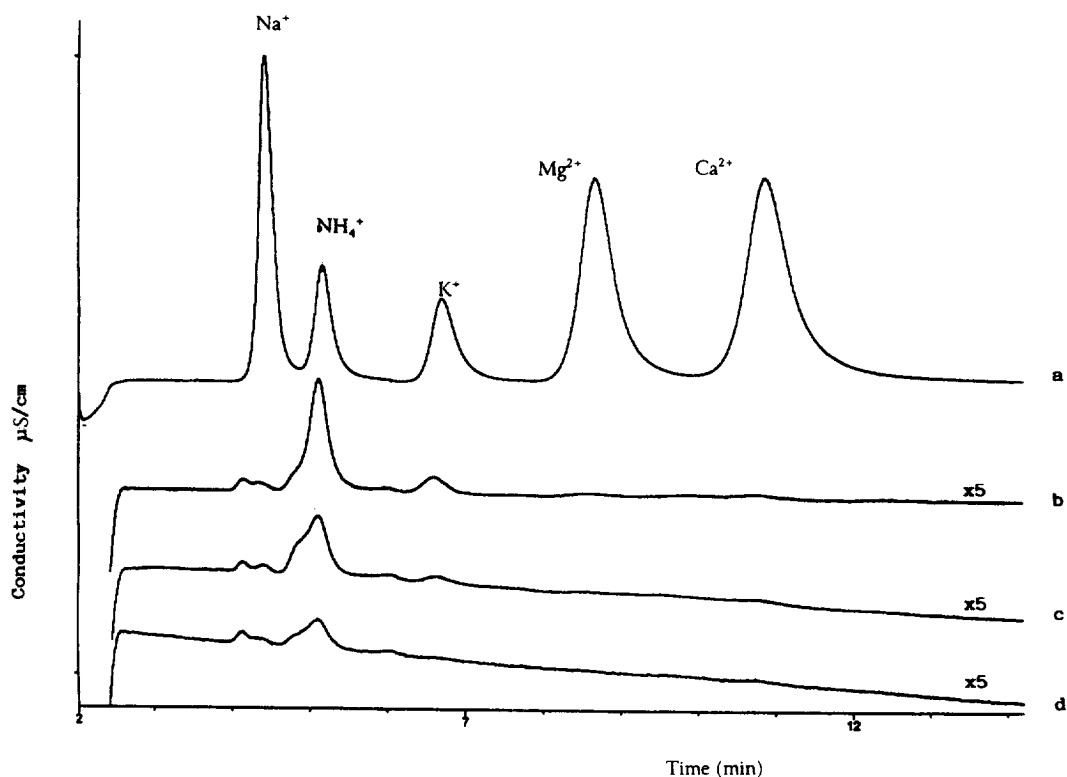


Fig. 3. Ultra-trace cation analysis: a=cation standard, $0.45 \mu\text{g/l}$ Na^+ , NH_4^+ , K^+ and Mg^{2+} and $0.9 \mu\text{g/l}$ Ca^{2+} ; b, c=Maxima product water; d=Maxima cartridge water.

time the purity of the product water is protected by the second cartridge which is effectively unexhausted. This is illustrated in Fig. 2.

Typical water obtained from this system was analysed by ion chromatography. A Dionex DX500 was used with a CD20 conductivity detector and a 250 mm×4 mm CS12 cation column. The eluent was 20 mM methanesulphonic acid at 1.2 ml/min. The water to be analysed was taken directly from the outlet of the water purifier. 20 ml of water was concentrated at 1 ml/min on a CG12 concentrator column using a DQP1 pump.

Calibration was carried out by serial dilution in ultra-pure water of a mixed cation standard containing 5 mg/l sodium, potassium, ammonium and magnesium and 10 mg/l calcium prepared from individual 1000 mg/l standards (Spectrosol, BDH, Poole, UK).

The calibration data are summarised in Table 2. The calibration slopes given are for best fit lines through the origin.

The calibrations are linear and the concentrations of the peaks found in the ultra-pure water can be estimated. These are summarised in Table 3 and examples of the peaks found shown in Fig. 3, along with those from one of the standards. Samples 2 and 3 are from the same unit taken on different days. Sample 4 is directly from a Maxima cartridge.

Concentrations found in the water from the Maxima are extremely low—less than 0.02 µg/l except for ammonium which is typically 0.06–0.11 µg/l. The source of the ammonium ions may be the resins or external contamination.

4. Conclusion

Resistivity is not a reliable indication of ionic concentrations below 1 µg/l.

The Maxima is designed to take advantage of the effectiveness of unexhausted premium grade ion-exchange resins at removing ions in order to guarantee ultra-low levels of ions in ultra-pure water.

Such high purity is needed for ultra-trace analysis by ion chromatography.

References

- [1] R.D. Thornton and T.S. Light, *Ultrapure Water*, 6, No. 5 (1989) 14–28.
- [2] K.T. Pate, *Ultrapure*, 8, No. 1 (1991) 26–33.
- [3] P. Whitehead, *Ultrapure Water*, 13, No. 6 (1996) 37–40.