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# Low-pressure ion chromatography

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**Abstract**

This paper describes the series of studies on low-pressure ion chromatography (LPIC), including its operating principle, distinguishing feature, Technology Index, and its application in analysis of acid rain, blood, oil field water and medicines etc.

## 1. Introduction

Ion chromatography (IC) first appeared in the mid-1970s [1] and has become highly developed in the last 10 years. At present, IC is operated with a high-pressure system, using a high-pressure pump to make the mobile phase flow through the separation column. The trend in IC has been a steady increase in the operating pressure (OP), *e.g.*, the Dionex Model 14 with OP 800 p.s.i. (1 p.s.i. = 6894.76 Pa), the 2000i series in the mid-1980s with OP 2000 p.s.i. and the present 4000i and 5000i series with OP 4000 and 5000 p.s.i., respectively.

We began to study IC in 1979 and devised low-pressure IC (LPIC) in 1985 [2]. Two kinds of instrument, "low-pressure fast analysis ion chromatograph" (LPFAIC) and "low-pressure transition metal ion chromatograph" (LPTMIC), were developed in 1988 and 1992, respectively. Both of them can be operated at a low pressure of $1.96 \cdot 10^5$–$2.94 \cdot 10^5$ Pa (30–40 p.s.i.).

When a conductivity detector is used, the former can measure $Li^+$, $Na^+$, $NH_4^+$, $K^+$, $Rb^+$, $Cs^+$, $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$ and $Ba^{2+}$ cations, inorganic anions such as haloides, $NO_3^-$, $PO_4^{3-}$, $SO_4^{2-}$ and $CO_3^{2-}$ and numerous organic acid ions. When combined with an optical detector, the latter can measure metal ions such as $Fe^{3+}$, $Cu^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Co^{2+}$, $Pb^{2+}$, $Fe^{2+}$, $Cd^{2+}$, $Mn^{2+}$, $Cr^{3+}$, $Cr^{6+}$, $Al^{3+}$ and $Zr^{3+}$ and $SiO_3^{2-}$, $S^{2-}$, $H_2PO_4^-$, phenol, salicylate, etc. Detailed studies of LPIC are described in this paper.

## 2. Experimental

### 2.1. Instrumentation

The ion chromatographs used in this work were a ZJ-1 LPFAIC and a ZJ-2 LPTMIC.

Figs. 1 and 2 show the flow systems of the LFAIC with a conductivity detector and the LPTMIC with an optical detector, respectively.

Instead of the separation column 4 shown in Fig. 2, a 30 mm × 0.5 mm I.D. PTFE tube is used to allow flow-injection analysis to be carried out. Placement of a concentration column at the position of the injection loop will permit on-line concentration and analyses for ultra-trace element components. Elution pump 2 and reaction

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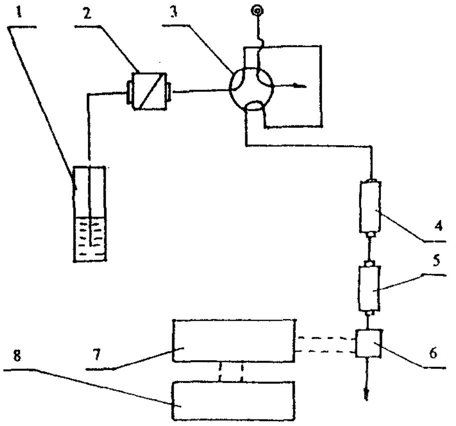

Fig. 1. Schematic diagram of the flow system of the LPFAIC. 1 = Eluent; 2 = low-pressure pump; 3 = injection valve; 4 = separation column; 5 = suppressor column; 6 = conductivity cell; 7 = detector; 8 = computer.

pump 6 shown in Fig. 2 can be replaced with a two-way low-pressure pump.

## 2.2. Reagents

Dilute nitric acid solutions were prepared from analytical-reagent grade concentrated nitric acid. Sodium carbonate solutions were prepared from analytical-reagent grade $Na_2CO_3$. Distilled, deionized water was used throughout.

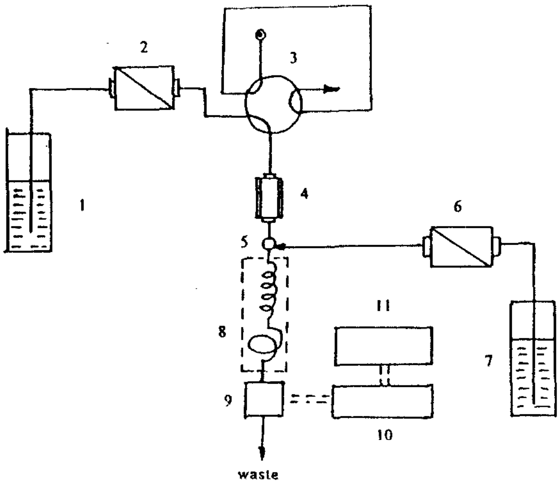

Fig. 2. Schematic diagram of the flow system of the LPTMIC. 1 = Eluent; 2,6 = low-pressure pumps; 3 = injection valve; 4 = separation column; 5 = mixer; 7 = chromogenic reagent; 8 = reaction coil; 9 = flow cell; 10 = optical detector; 11 = computer.

## 2.3. Main chromatographic conditions

The conditions were as follows: for the determination of alkali metals and $NH_4^+$, eluent $1.44 \cdot 10^{-3}$ mol/l $HNO_3$, column $C_1$ (30 mm × 5 mm I.D.), flow-rate 0.8–1.0 ml/min, conductivity detector and single-column system; for the determination of alkaline earth metals, eluent $6.0 \cdot 10^{-4}$ mol/l ethylenediamine–$8.0 \times 10^{-4}$ mol/l citric acid, column $C_2$ (30 mm × 5 mm I.D.), flow-rate 0.8–1.0 ml/min, conductivity detection and single-column system; for the determination of anions, eluent $2.0 \cdot 10^{-3}$ mol/l $Na_2CO_3$, low-pressure anionic column (60 mm × 6 mm I.D.), flow rate 1.0 ml/min, conductivity detection and double-column system; for the determination of organic acids, eluent $1.0 \cdot 10^{-4}$–$7.2 \cdot 10^{-4}$ mol/l $HNO_3$, low-pressure organic acid column (100 mm × 6 mm I.D.), flow-rate 0.4–0.6 ml/min, conductivity detection and single-column system; for the determination of $Cu^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Co^{2+}$, $Pb^{2+}$ and $Fe^{2+}$, eluent 0.02 mol/l oxalic acid–0.02 mol/l citric acid, column $C_3$ (40 mm × 5 mm I.D.), optical detection at 520 nm and postcolumn reaction system; and for the determination of $Zn^{2+}$, $Pb^{2+}$, $Fe^{2+}$, $Cd^{2+}$, $Mn^{2+}$, eluent tartaric acid–citric acid, column $C_3$ (40 mm × 5 mm I.D.), optical detection at 520 nm and postcolumn reaction system.

# 3. Results and discussion

## 3.1. Operating principle

Instead of a high-pressure pump, a low-pressure pump is adopted to transmit the eluent. After the ions to be measured have passed through the low-pressure column at a low pressure of $1.96 \cdot 10^5$–$2.94 \cdot 10^5$ Pa they are separated efficiently by ion-exchange equilibrium. The detection and determination of alkali metal, alkaline earth metal and inorganic anions and other numerous organic ions can be achieved using a conductivity detector with a unique, jetformed structure conductivity cell. For the measurement of transition metal ions, postcolumn derivatization is helpful to allow the ions to react with coloured material in the postcolumn mixer and the reaction coli. An optical detector can then be used for the determination.

The separation principle of the LPIC column is mainly based on rapid ion exchange (organic acid based on ion exclusion) on the surface of the resin particles. The principle of the dynamics is membrane broadening and that of conductivity detection is based on the formation of ions of the ionic material in the aqueous solution to produce conductivity. Changes in ion concentration are converted into conductivity signals, which are recorded by a computer or a recorder.

With visual photometric detection, after separation in the column, the ions to be measured enter the postcolumn mixer and mixed with a postcolumn chromogenic reagent, resulting in the formation of a coloured chelate, the concentration and absorbance of which are linearly related. The concentration of the metal ions can thus be measured.

### 3.2. *Investigation of the technique*

The replacement of the high-pressure pump with a low-pressure one decreases the problems of leakage and blockage, etc., and results in high performance at low pressure. To establish why LPIC can be carried out at such a low pressure as 30–40 p.s.i. with excellent efficiency we consider mainly the following aspects.

A series of packings for low-pressure use were developed through several years of investigation. The technique for making these special packings is different from that for packings for high-pressure IC. An LPIC packing has the advantages of low capacity, excellent dynamic performance and rapid mass-transfer ability.

The packing for the cation-exchange separation column in LPIC consists of round-shaped particles of ion exchanger. There is a very thin covering of ion exchanger with an inert nucleus in the centre. The exchange capacity is 0.012 mequiv./g. The packing of the anion-exchange separation column for LPIC is also a sort of round ion exchanger with exchange capacity 0.015 mequiv./g.

The LPIC columns used in the separation of organic acids employ an $H^+$ cation exchanger as packing material, with a particle diameter of 15–20 μm and an exchange capacity of 4 mequiv./g.

Very short columns are used, the length being only 30 mm, whereas that of a high-pressure IC column is 250–500 mm. The effusive conductivity cell, of novel design, has an electrode at the solution entry end. The ions to be measured are effused directly to the opposite electrodes, so a much higher sensitivity can be achieved. The dead volume is only 1 μl which is much less than that of HPIC conductivity cells (usually 5 μl). It also has the advantages of no dead-angle, easy air removal, low interference of the flow stream and low baseline drift and noise. Fig. 3 shows the construction of the LPIC conductivity cell.

### 3.3. *Development of LPIC postcolumn reaction system*

In the postcolumn system in high-pressure IC, a steel nitrogen bottle is needed to provide pressure to transport the reaction solution. In our method, only a two-way pump is used, without the requirement for any all-plastic high-pressure pump, a large-volume steel nitrogen bottle, a pressure-reducing value, a one-way valve or a buffer valve.

In addition to its use in IC analysis, LPIC can also be applied with flow-injection analysis, whereas high-pressure IC cannot.

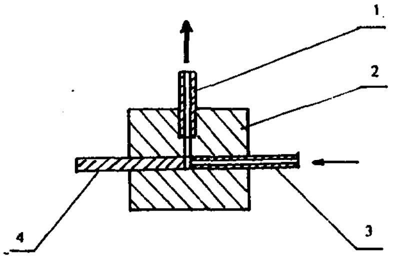

Fig. 3. Construction of LPIC conductivity cell 1 = Exit of solution; 2 = cell body; 3 = entry of solution (an electrode); 4 = second electrode.

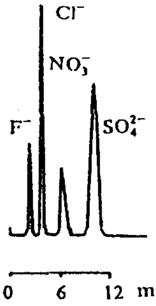

Fig. 4. Analysis of acid rain.

The detection limit for each ion is generally $\leq 10^{-9}$ g/ml. Both the baseline noise and drift are very low. LPIC also has the merits of small volume, low mass (one tenth of that in high-pressure IC), low cost and easy maintenance.

### *3.4. Application of LPIC*

Chromatograms obtained in the analysis of various types of samples are shown in Figs. 4–9. Details of some analyses are given below.

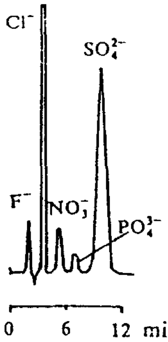

Fig. 5. Analysis of Chengdu tannery waste water.

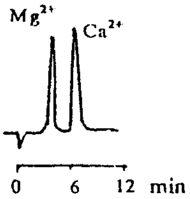

Fig. 6. Analysis of river water.

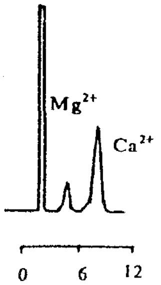

Fig. 7. Analysis of acid rain. Concentrations: $Mg^{2+}$ 0.4 μg/ml and $Ca^{2+}$ 1.0 μg/ml.

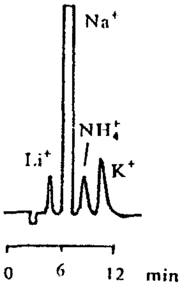

Fig. 8. Analysis of oilfield water.

*Analysis acid rain*

Standard US EPA (Environmental Protection Agency) samples prepared for the WMO (World Meteorological Organization) were analysed and the results were compared with the stated values (which were not known to us prior to the analyses).

The results agreed well (Table 1). A comparison made by the Atmospheric Laboratory of the Chinese Academy of Meteorology Science with statistical data from the 7th International

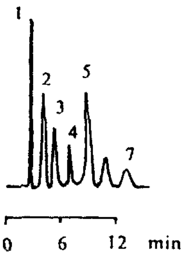

Fig. 9. Analysis of tobacco. Peaks: 1 = inorganic acid; 2 = lactic acid; 3 = formic acid; 4 = succinc acid; 5 = acetic acid; 6 = propionic acid; 7 = butyric acid.

Table 1
Comparison of US EPA values and LPIC results

| Ion | Series No. | EPA value ($\mu$g/ml) | LPIC result ($\mu$g/ml) |
|---|---|---|---|
| $Na^+$ | 1313 | 0.185 | 0.18 |
| | 2026 | 0.241 | 0.29 |
| | 3286 | 0.490 | 0.49 |
| $NH_4^+$ (as N) | 1313 | 0.083 | 0.084 |
| | 2026 | 0.627 | 0.613 |
| | 3286 | 0.798 | 0.761 |
| $K^+$ | 1313 | 0.066 | 0.08 |
| | 2026 | 0.094 | 0.10 |
| | 3286 | 0 094 | 0.10 |

Rainfall Chemistry Analysis Results of the 38 Laboratories of BAPMoN (Background Air Pollution Monitor Net of WMO) confirmed that the accuracy of the LPIC analyses corresponded to the average accuracy obtained by the 38 international laboratories.

*Analysis of blood [3]*

Measurement of $Na^+$, $K^+$ and $Cl^-$ in fourteen samples of human serum provided by the Medical University of West China by LPIC gave results very close to those obtained using a Beckman E4A instrument with ion selective electrodes. One of the fourteen samples was injected successively twelve times to determine the accuracy of the LPIC method and the relative standard deviation was 1.2%. The results indicate that LPIC has a high sensitivity and with its easy operation it can be widely used in clinical medicine.

*Measurement of oilfield water*

The results for the determination of $Fe^{2+}$, $Zn^{2+}$ and $Mn^{2+}$ in oilfield water are given in Table 2 and compared with those obtained using a Jarrell-Ash ICAP9000 (N + M) inductively coupled plasma atomic emission spectrometer.

The results given by the two methods agreed well. Recovery experiments showed that the

Table 2
Comparison of LPIC and ICP results for oilfield water

| Series No. | Methods | $Fe^{2+}$ ($\mu$g/ml) | $Zn^{2+}$ ($\mu$g/ml) | $Mn^{2+}$ ($\mu$g/ml) |
|---|---|---|---|---|
| 18 | ICP | 0.59 | 9.14 | 5.17 |
| | LPIC | 0.60 | 9.21 | 5.00 |
| 80 | ICP | 0.31 | 10.7 | 5.59 |
| | LPIC | 0.36 | 10.5 | 5.50 |
| 46 | ICP | 1.16 | 7.70 | 3.70 |
| | LPIC | 1.10 | 7.53 | 3.90 |
| 9 | ICP | 0.30 | – | 0.025 |
| | LPIC | 0.50 | – | 0.030 |
| 36 | ICP | 0.92 | – | 0.020 |
| | LPIC | 0.83 | – | 0.030 |

recoveries of $Fe^{2+}$, $Zn^{2+}$ and $Mn^{2+}$ in oilfield water by LPIC are between 94 and 105%.

*Analysis of medicines*

Using LPIC, samples provided by the Medicines Institute of the Medical University of West China were analysed as follows: measurement of the content of nitrate and sulphate in the inorganic medical carbon, magnesium silicate and the organic medical methoxyestrone (OPC-8212) and measurement of the content of related elements in the medical $Li_2CO_3$ and KCl which contain lithium, fluorine and chlorine. The results were similar to the data in the Chinese Pharmacopoeia.

The following medicines were also analysed by LPIC: measurement of trace $Zn^{2+}$ in insulin, providing results in agreement with the Chinese Pharmacopoeia but much faster and more easily way than by the stipulated method; and measurement of zinc gluconate content, giving a result close to that obtained with by the standard method of the National Hygiene Department.

Measurement of zinc gluconate particulate reagent in abundant blood syrup (a blood tonic made in China) gave a recovery between 96 and 105.3%. Owing to the high sensitivity and small injection volume with LPIC, the sample need not be pretreated. Also, there is no interference with the measurement from the matrix.

## 4. Acknowledgement

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