Journal of Chromatography A, 1436 (2016) 59–63

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

# Enhanced methodology for porting ion chromatography retention data

Soo Hyun Park[a], Robert A. Shellie[a], Greg W. Dicinoski[a], Georg Schuster[a], Mohammad Talebi[a], Paul R. Haddad[a,*], Roman Szucs[b], John W. Dolan[c], Christopher A. Pohl[d]

[a] Australian Centre for Research on Separation Science (ACROSS), School of Physical Sciences-Chemistry, University of Tasmania, Private Bag 75, Hobart 7001, Australia
[b] Pfizer Global Research and Development, Sandwich, UK
[c] LC Resources Inc., 1795 NW Wallace Rd., McMinnville, OR 97128, USA
[d] Thermo Fisher Scientific, Sunnyvale, CA, USA

ARTICLE INFO

*Article history:*
Received 6 November 2015
Received in revised form 7 January 2016
Accepted 7 January 2016
Available online 16 January 2016

*Keywords:*
Ion chromatography
Porting
Simulation of separations
Method translation
Prediction of retention times

ABSTRACT

Porting is a powerful methodology to recalibrate an existing database of ion chromatography (IC) retention times by reflecting the changes of column behavior resulting from either batch-to-batch variability in the production of the column or the manufacture of new versions of a column. This approach has been employed to update extensive databases of retention data of inorganic and organic anions forming part of the "Virtual Column" software marketed by Thermo Fisher Scientific, which is the only available commercial optimization tool for IC separation. The current porting process is accomplished by performing three isocratic separations with two representative analyte ions in order to derive a porting equation which expresses the relationship between old and new data. Although the accuracy of retention prediction is generally enhanced on new columns, errors were observed on some columns. In this work, the porting methodology was modified in order to address this issue, where the porting equation is now derived by using six representative analyte ions (chloride, bromide, iodide, perchlorate, sulfate, and thiosulfate). Additionally, the updated porting methodology has been applied on three Thermo Fisher Scientific columns (AS20, AS19, and AS11HC). The proposed approach showed that the new porting methodology can provide more accurate and robust retention prediction on a wide range of columns, where average errors in retention times for ten test anions under three eluent conditions were less than 1.5%. Moreover, the retention prediction using this new approach provided an acceptable level of accuracy on a used column exhibiting changes in ion-exchange capacity.



## 1. Introduction

Method translation or method transfer in chromatographic analysis has become an area of increasing interest. Numerous studies regarding method transfer have been reported in the area of liquid chromatography (LC) [1,2] as well as gas chromatography (GC) [3,4]. Method translation in GC is described as the rescaling of method parameters (temperature programs, pressures, etc.) as well as GC components (carrier gases, columns, detectors, etc.) without losing the peak elution pattern [3]. This can lead to the improvement of chromatographic performance in areas such as sample capacity, analysis time, and peak resolution through simple rescaling, along with the reduction of the development time and cost required for the creation of a desired chromatographic analysis method.

Recently, the concept of method transfer has been introduced to update extensive retention databases embedded in the "Virtual Column®" software, using the so called "porting" methodology [5]. The Virtual Column software allows the simulation of ion chromatography (IC) separations performed under a wide range of experimental conditions (e.g. analytes of interest, eluent type, column type, temperature, flow-rate) in order to identify the optimal eluent and column conditions for a desired separation. This simulation is based on the application of mathematical retention models

*Abbreviations:* CPM, current porting method; MPM, modified porting method; MAPE, mean absolute percentage error.

* Corresponding author. Fax: +61 3 62262858.
*E-mail address:* paul.haddad@utas.edu.au (P.R. Haddad).

http://dx.doi.org/10.1016/j.chroma.2016.01.031
0021-9673/

applied to an extensive database of experimentally-determined analyte retention data embedded in the software [6]. This database covers over 150 anions, cations, and carbohydrate species as analytes, 21 columns, 6 eluent types, 2 column diameters, and 2 temperatures, comprising in total 23,040 datapoints. It is the wide scope of this database which makes Virtual Column such a powerful tool for the development of IC separation methods, but in turn it is also the validity of these retention data which determines the accuracy of the simulated chromatograms. This retention database was constructed around 10 years ago, so the simulation and optimization for IC separations can cause errors when the predicted separations are applied on recently produced columns. These errors can result from changes in column behavior due to either batch-to-batch variability in the production process or the manufacture of new column versions. Errors can also result when the predicted separations are applied to used columns which may have a different ion-exchange capacity to the column on which the original retention data were acquired. With this in mind, a porting methodology to update the retention databases was developed to improve the accuracy of retention prediction by reflecting column-related changes, such as ion-exchange capacity [5].

According to our previously developed porting methodology [5], the retention data embedded into Virtual Column are recalibrated for the entire set of analytes on each particular column by using porting equations which relate existing (or embedded) data to new retention data. In this porting method, new retention data were obtained experimentally by conducting isocratic separations using two representative ions (chloride and thiosulfate) on a new column under three eluent concentrations. Porting equations describing the changes in retention data for these two ions are then derived and are applied to all ions in the database. The general principle of this approach is that any changes in retention observed for chloride and thiosulfate can be generalized across all ions in the database. It has been found that although the porting procedure generally improved the retention prediction accuracy on new columns such as AS20 and AS11HC columns, the retention prediction accuracy for some columns such as AS19 column was poorer than expected. We attribute this to some deficiencies in the porting procedure.

In this study, we have improved the accuracy of the porting procedure by increasing the number of marker anions used to derive the porting equations from two to six. Subsequently, we have validated the modified porting method (MPM) using three newly manufactured Thermo Fisher Scientific columns (AS20, AS19, and AS11-HC). For the validation, the values of mean absolute percentage errors (MAPEs) in the prediction of the retention times were compared in terms of the data types (original embedded data, ported data using the current porting method (CPM), and ported data using the MPM) employed by the mathematical retention model. The accuracy of the retention prediction was then illustrated by plots which show predicted versus measured retention times. Finally, isocratic separations for 13 ions were performed on an AS20 column which had been used for around more than 1500 runs, under three different eluent concentrations. The MPM resulted in a more precise and robust recalibration technique for the update of the retention databases on a wide range of columns compared to the CPM.

## 2. Materials and methods

### 2.1. General

The isocratic retention data used in this work, which are embedded in the Virtual Column software, had been acquired previously as outlined in Ref. [7]. These isocratic data were collected at different times using different instruments and columns from different manufacturing batches. Therefore, any comparisons of data made between the isocratic measurements will include variability between instruments and column batches.

### 2.2. Reagents and solutions

Standard solutions of the test anions were prepared by dissolution of their corresponding potassium, sodium, or ammonium salts of analytical reagent grade in Milli-Q water (18.2 MΩ; Merck-Millipore, Bayswater, Australia). The following anion standard solutions were prepared from their sodium salts: fluoride, chlorate, malonate, oxalate, succinate, and sulfate (BDH, Melbourne, Australia); carbonate and nitrite (AJAX, Sydney, Australia); iodide, and thiosulfate (Aldrich, Sydney, Australia); bromide, molybdate, perchlorate and phosphate (Sigma, Sydney, Australia). Chloride and formate anion standard solutions were prepared from their ammonium salts purchased from BDH and Sigma, respectively. The remaining anion standard solutions were prepared from their potassium salts: chromate and nitrate (BDH), and bromate, and thiocyanate (AJAX).

### 2.3. Instrumentation

All analyses were carried out using a Dionex (Sunnyvale, CA, USA) ICS-3000 Ion Chromatography system consisting of dual gradient pump unit (Dionex ICS-3000 DP), dual eluent generator unit (Dionex ICS-3000 EG), dual suppressed conductivity detector compartment (Dionex ICS-3000 DC) and autosampler (Dionex AS). Separation was performed on Dionex IonPac AS20, AS19, and AS11HC columns (all 250 mm × 4 mm i.d.) with their associated guard columns (all 50 mm × 4 mm i.d.) at column temperature of 30 °C. A Dionex EluGen® cartridge (EGC II KOH) followed by a Dionex CR-ATC ion trap column were employed to generate electrolytically each eluent composition and a Dionex ASRS 300 4 mm suppressor was used for eluent suppression. The analytes were detected by suppressed conductivity at 35 °C. An injection volume of 10 μL and an eluent flow-rate of 1.0 mL/min were used throughout this work. Instrument control and data acquisition were performed using Chromeleon® chromatography management software (version 6.80). The following eluent compositions were used to collect isocratic data for the porting and its validation on desired column: 20, 35, and 65 mM hydroxide eluents on AS20 column; 15, 25, and 40 mM on AS19 column; 16, 30, 45 mM on AS11HC. All experimental points were carried out in triplicate, of which the averaged values were used as the experimental data.

### 2.4. Void time measurement

The column void time $t_0$ for the derivation of the porting equations in this work was carefully obtained from the minimum in the water dip peak by using the following equation:

$$t_0(\text{column}) = t_0(\text{analyticalcolumn} + \text{guardcolumn} + \text{tubingexistingintheICsystem}) - t_0(\text{tubingexistingintheICsystem}) \quad (1)$$

The extra column void time, $t_0$ (tubing existing in the IC system) in Eq. (1), was added back after calculation of the predicted retention times for analytes.