



# Expanding the elution by characteristic point method to columns with a finite number of theoretical plates



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## ARTICLE INFO

### Article history:

Received 17 April 2015

Received in revised form 10 August 2015

Accepted 12 August 2015

Available online 15 August 2015

### Keywords:

Single component adsorption

Adsorption isotherm

Elution by characteristic point method

Dispersion

Number of theoretical plates

## ABSTRACT

The elution by characteristic point (ECP) method provides a rapid approach to determine whole isotherm data with small material usage. It is especially desired wherever the adsorbent or the adsorbate is expensive, toxic or only available in small amounts. However, the ECP method is limited to adsorbents that are well optimized for chromatographic use and therefore provide a high number of theoretical plates when packed into columns (2000 or more for Langmuir type isotherms are suggested). Here we present a novel approach that uses a new profile correction to apply the ECP method to poorly optimized adsorbents with less than 200 theoretical plates. Non-ideality effects are determined using a dead volume marker injection and the resulting marker profile is used to compensate the named effects considering their dependency from the actual concentration instead of assuming rectangular profiles. Experimental and literature data are used to compare the new ECP approach with batch method results.

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## 1. Introduction

Chromatography and adsorption are two separation techniques that are widely used for analytical and preparative tasks. Both techniques are based upon an accumulation of a preferred component on the surface of an adsorbent relative to its concentration in the bulk fluid phase. The relationship between the concentration in the fluid and on the surface of the adsorbent is quantified by adsorption isotherms. For this reason, the determination of adsorption isotherms is essential for the application of both, adsorption and chromatography.

There are various methods known to determine adsorption isotherms. All of them have advantages and disadvantages in terms of time and material consumption, accuracy, applicability for single or multi component systems etc. [1,2]. On the one hand, the static batch method is a straightforward approach where a fluid with an initial concentration of a substance is mixed with the adsorbent. After equilibration, the final concentration is measured and the loading of the adsorbent can be calculated by closing the overall mass balance. Hence, there are no more conditions that have to be fulfilled and the method can be applied to almost every system, where the overall mass balance can be closed. However, the

batch method does only provide one point of an isotherm per batch leading to a thin distribution of points with a high consumption of time and material [3,4]. On the other hand, dynamic methods require the differential establishment of equilibrium and thus can only be applied to packed columns. In these methods, a column is first equilibrated with a certain inlet concentration. Afterwards, the equilibrium is disturbed with a pulse and the response of the system is detected. Various methods are known that differ in the initial inlet concentration and the size of the disturbance resulting in different material consumption and accuracy [1,5]. Two of these methods are particularly suitable for minimizing the material consumption as a single pulse experiment delivers the whole isotherm data [1]. In the Inverse Method (IM), an adsorption isotherm model is assumed and model parameters are extracted from a fit of the predicted elution profile to the experimental data [1]. This approach therefore delivers the optimum set of model parameters for a given adsorption equilibrium model but not the original adsorption equilibrium data points. However, it has been shown that the IM results in equilibrium information that may be used for process optimization studies [7]. In the Elution by Characteristic Point (ECP) method, the diffusive part of an elution profile is used to calculate the adsorption isotherm in a direct way. The ECP method uses only basic arithmetical operations to calculate the loading and therefore provides the original adsorption equilibrium data.

Basically, the ECP method can be used for type I or type III adsorption isotherms and has been expanded for the determination of various other types [8]. The diffusive parts of an elution profile are used to calculate isotherm data whereas the information

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in shock fronts is lost. Moreover, there have been developments to improve the accuracy of the ECP method in recent years. Mainly the cut-injection technique was established to generate a more rectangular injection profile [9] and the ECP-slope approach eliminates the difficulties to find the starting point of the integration [10].

However, the ECP method is based on the ideal model of chromatography assuming infinite column efficiency equivalent to an infinite length of the column. This corresponds to a very high number of theoretical plates ( $N_t$ ) with an increase in uncertainty when  $N_t$  is reduced. Previous analyses have shown that the required number of theoretical plates depends on the isotherm model that is used. For a Langmuir model with a homogenous surface the number of theoretical plates should be at least 2000 to reduce the error to less than 3% and at least 5000 to reduce the error to less than 5% for a heterogeneous surface described by the bi-Langmuir model [11,12]. Even though such values for  $N_t$  are achievable with adsorbents that are optimized for the use in chromatographic columns, they cannot be reached with every adsorbent or column. Specifically in early stages of process development or in situation with a very limited availability of adsorbent, eluent and/or value component, non-optimized combinations of separation phases and column equipment may have to be used. This will result in deviations of the real column performance from the ideal assumptions underlying the ECP method, resulting in numbers of theoretical plates significantly smaller than required in the original ECP method.

This contribution therefore proposes an approach that allows to expand the applicability of the ECP method to situations where the actual number of theoretical plates is one or two orders of magnitude smaller without compromising on uncertainty in the equilibrium information. By that, we expand the possibilities for isotherm determination with dynamic methods to a significantly broader range of adsorbent/column systems. Specifically, it expands the use of the ECP method to situations with a very limited availability of adsorptive and/or adsorbent material, typically encountered at early stages of new product or process development or for very costly substances.

## 2. Experimental

### 2.1. Chemicals

Acetonitrile (HPLC-grade, VWR International LLC, Radnor, PA, USA), dealuminated  $\beta$ -zeolite extrudate with Si/Al=75 called BEA150 extrudate (Clariant International Ltd, Muttenz, Switzerland), sodium chloride (Sigma-Aldrich Corporation, St. Louis, MO, USA), disodium phosphate (Carl Roth GmbH + Co. KG, Karlsruhe, Germany), fructose, glucose, monopotassium phosphate, sucrose and sorbitol from Roth were used as received. Water was prepared by double distillation.

### 2.2. Apparatus and instrument

Dynamic method experiments were carried out with a HPLC system including a HPLC pump 2248 (Pharmacia Corp., Uppsala, Sweden), a degasser GT0280 (Techlab GmbH, Braunschweig, Germany), an injector 7125 (VWR) with a 100  $\mu$ L injection loop and an UV-detector L-7420 (Hitachi Ltd., Chiyoda City, Japan) at room temperature. Stainless steel columns with different dimensions of 50 mm  $\times$  4 mm, 100 mm  $\times$  3.2 mm and 100 mm  $\times$  2.1 mm (length/diameter) were used. Dead volume  $V_0$  was determined to be 0.69 mL, 0.76 mL and 0.51 mL, respectively.  $V_0$  was determined using the elution time of the sucrose peak. Flow rate was 200, 112 and 56  $\mu$ L/min for the columns with 4, 3.2 and 2.1 mm diameter, respectively. Thus, superficial velocity was about 16 mm/min for the columns with 2.1 and 4 mm diameter and about 14 mm/min

for the other column. The number of theoretical plates for the packed columns was determined using the internal calculation of the chromatography software (Clarity 4 from Data Apex, Prague, Czech Republic).

### 2.3. Methods

Zeolite extrudate was crushed with a planetary ball mill, sieved with a nominal fineness of 100  $\mu$ m and particle size distribution was measured with HELOS KR (Sympatec GmbH, Clausthal-Zellerfeld, Germany). 21.3 g of disodium phosphate and 20.5 g of monopotassium phosphate were filled up to 1 L with double distilled water to produce 0.3 M phosphate buffer at pH 7.0.

For dynamic methods, crushed extrudate was manually weighed into the columns and columns were purged with solvent until the detector signal was stable. Then, injections of marker and adsorbate solutions were fed for ECP method and Peak Maximum (PM) method. PP method was carried out using solutions containing 5 to 50 g/L Sorbitol to establish the concentration plateau. Subsequently, injections of solutions, that contained 2.5 g/L less Sorbitol than the eluent, were used to disturb the equilibrium.

Batch adsorption was conducted in 2 mL micro tubes with a zeolite concentration of 200 g/L. Tubes were shaken with a Thermomixer comfort (Eppendorf, Hamburg, Germany) at 20 °C and 1000 rpm. After 20 h, zeolites were separated by centrifugation for 10 min at 16,100 g with miniSpin (Eppendorf). The supernatant was analyzed using HPLC with a YMC Polyamine II, 5  $\mu$ m, 12 nm, 150  $\times$  4.6 mm column (YMC Co., Ltd., Kyoto, Japan) at 30 °C and a refractive index detector RI-101 (Showa Denko, Tokyo, Japan). The eluent was acetonitrile-water (75:25, v/v) with a flow rate of 1 mL/min. Injection volume was 20  $\mu$ L.

## 3. Theory

### 3.1. Batch method

As stated in section 1 the overall mass balance is used to calculate loadings from raw data generated by the batch method:

$$q_i^{Ex} = \frac{(c_i - c_e)}{m_{Ad}} V_L \quad (1)$$

where  $q_i^{Ex}$  is the adsorption excess,  $V_L$  is the liquid volume,  $m_{Ad}$  is the mass of adsorbent and  $c_i$  and  $c_e$  are the initial and end concentrations, respectively. This formula has to be expanded due to the fact, that the solvent can be adsorbed in a significant amount especially when weak interacting substances are investigated [4,13,14]. Therefore, it is considered that the solvent and the investigated substance show similar adsorption behavior regarding their mass. Then exclusion experiments with substances that cannot enter the pores can be carried out to determine a saturation loading  $q_s$ . This leads to the absolute loading  $q_i$  that also accounts for the adsorption of solvent:

$$q_i = \frac{c_i - \left(1 - q_s \frac{m_{Ad}}{m_0}\right) c_e}{m_{Ad} \left(\frac{1}{V_L} + \frac{1}{m_0} c_e\right)} \quad (2)$$

with the mass of liquid  $m_0$ .

### 3.2. ECP method

The ECP method is directly deduced from the ideal model of chromatography. Therefore, a brief description of the current approach for ECP method is given. Then, the actual modifications made in this work are described in detail. Moreover, the concept of the number of theoretical plates and its calculation are presented,

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