



# Bromate peak distortion in ion chromatography in samples containing high chloride concentrations



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## ABSTRACT

In this study, the effect of column overload of the matrix ion, chloride, on the elution peak profiles of trace bromate is investigated. The resultant peak profiles of chloride and bromate are explained on the basis of competitive Langmuir isotherms. The Thermo IonPac AS9-HC, AS19 and AS23 columns are recommended by the manufacturer for bromate (a carcinogen) analysis. Under trace conditions, these columns provide baseline resolution of bromate from matrix ions such as chloride ( $R_s = 2.9, 3.3$  and  $3.2$ , respectively for the three columns). Injection of 10–300 mM chloride with both hydroxide and carbonate eluents resulted in overload on these columns. On the basis of competitive Langmuir isotherms, a deficiency in the local concentration of the more retained eluent in addition to analyte overload leads to fronting of the overloaded analyte peak. The peak asymmetries ( $B/A_{10\%}$ ) for chloride changed from 1.0 (Gaussian) under trace conditions to 0.7 (fronting) at 300 mM  $Cl^-$  for IonPac AS9-HC, 0.9–0.6 for AS19 and 0.8–0.5, for AS23, respectively. The 10 mM bromate peak is initially near Gaussian ( $B/A_{10\%} = 0.9$ ) but becomes increasingly distorted and pulled back into the chloride peak as the concentration of chloride increased. Increasing the eluent strength reduced the pull-back effect on bromate and fronting in chloride in all cases.

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## 1. Introduction

Ion chromatography (IC) is the most established and robust analytical technique for the analysis of inorganic and organic anions. Routine application of IC is found in the environmental, chemical, power and pharmaceutical industries [1–3]. A wide variety of IC columns with different packing materials and functionalities have been manufactured to cater to these analytes, with >70 columns currently available [4].

A trend in IC column development has been to increase the column capacity from 40 and 2800  $\mu\text{eq}/\text{column}$  [5]. This greater capacity enables analysis of ions of greater difference in concentration [6,7]. Despite this, overload effects (i.e., non-Gaussian peaks) are observed when high concentrations of sample are injected [8]. These effects and their occurrence can best be explained on the basis of a competitive Langmuir isotherm [8,9]. Overloaded analyte peaks are tailed when the analyte is more strongly retained than the eluent (e.g., eluting  $Br^-$  with borate), and fronting when the analyte is more weakly retained than the eluent (e.g.,  $Br^-$  with

$HCO_3^-/CO_3^{2-}$ ) [7] and there is a localized deficiency of the eluent [10].

A second trend has been an increase in the hydrophilicity of the ion exchange sites [7,11–13]. The relative retention of the analyte and  $OH^-$  has consequences for the type of overload observed. If the analyte is more retained than hydroxide ion (e.g.,  $Br^-$  on the AS16 column), then overload of analyte results in tailed peaks [8]. Alternately, if the analyte is less retained than hydroxide (e.g.,  $Br^-$  on the IonPac AS18 column) [8] and there is a local deficiency of eluent [10], then overload of analyte results in fronting peaks. While the peak shape of the overloaded ion is well understood, the impact of the overload by a matrix ion on nearby trace ions has not been investigated.

In environmental samples, the high concentration matrix ions exhibit overloaded non-Gaussian peak profiles that can severely distort analyte peak(s) of interest [7,12,14,15]. Of particular interest, and the reason for this work, is to investigate the analyte peak distortion for trace bromate in high ionic strength samples, and to determine how the matrix affects the analyte peak distortion, and the criteria for minimizing this effect.

Bromate ( $BrO_3^-$ ) usually occurs in trace concentrations in finished water and groundwater systems [14].  $BrO_3^-$  is an oxyanion by-product formed by ozonation or chlorination of water supplies containing inorganic bromide ( $Br^-$ ) [16,17]. Bromate has been

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classified as a possible human carcinogen by the World Health Organization (WHO), who recommended  $\leq 10 \mu\text{g/mL}$  bromate in drinking water [17–19]. However, the matrix ions may be present at concentrations 1000 to 100,000 times higher than that of  $\text{BrO}_3^-$ , making quantitative analysis of  $\text{BrO}_3^-$  by direct injection in IC very difficult [16,18,20,21]. The objective of this work is to investigate the peak shape caused by matrix (i.e.,  $\text{Cl}^-$ ) overload on columns commonly used for  $\text{BrO}_3^-$  analysis, and how that matrix overload affects the shape of the trace bromate peak.

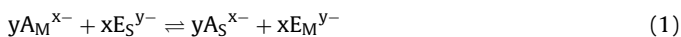
## 2. Theory

### 2.1. Concept of non-linear isotherm

Gaussian analyte peak profiles in HPLC result when the column is operating under linear isotherm conditions [22]. Concentration overload conditions result in a deviation from the Gaussian peak profile (linear) to non-linear isotherm peak profiles. The shape of the analyte peak is related to its concentration in the stationary phase ( $C_S$ ) vs. the analyte concentration in the mobile phase ( $C_M$ ). [23,24]. A plot of  $C_S$  vs.  $C_M$  is referred to as a sorption isotherm. The common types of non-linear isotherms include the convex-shaped Type I isotherms, S-shaped Type II isotherms, and the concave-shaped Type III isotherms [25]. Type I isotherms often result in tailing peaks, whereas the Type III isotherms result in fronting peak [26,27]. Unusual peak shapes including split peaks and peaks with secondary humps result from Type II isotherms [8,9]. Predicting and describing the band shape of sorption isotherms under overload conditions can involve extensive numerical modeling and optimization [28].

### 2.2. Concept of competitive Langmuir isotherm

The fundamental equilibrium in IC is [1,29–31]:



where eluent ion  $E^{y-}$  and the analyte ion  $A^{x-}$  compete for ion exchange sites on the stationary phase (subscript S).

Under concentration overload conditions either tailing or fronting peak are observed in IC [8]. This behavior has been explained on the basis of a competitive Langmuir isotherm [8]. The competitive Langmuir adsorption isotherm is the most common model for non-linear adsorption chromatography [26,28,32]. The competitive Langmuir isotherm for the  $k^{\text{th}}$  component of  $n$  components can be given as:

$$\frac{q_k}{q_s} = \frac{b_k C_k}{1 + \sum_{k=1}^n b_k C_k} \quad (2)$$

where  $q_k$  is the amount of adsorbed component (analyte or mobile phase component) at equilibrium with stationary phase versus the saturation capacity  $q_s$  of the given component,  $b_k$  is the equilibrium constant of the component, and the denominator is the sum total of all components sorbing onto the stationary surface [7]. Whether tailing or fronting is observed under overload conditions depends in part on the relative retention of the overloaded analyte and the eluent [8,13,26,28] on the stationary phase. In IC under overload conditions, peak tailing is observed if the analyte is more strongly retained than the eluent. Peak fronting is seen if the analyte is more weakly retained than the eluent [8], and if there is a localized deficiency of the eluent [10].

If a second analyte is present, its peak may be distorted or moved due to the overloaded peak [22,33,34]. Consider a two-component system in which the two peaks are baseline resolved under trace conditions. First, we will discuss the impact if overload of one component causes a tailed peak (convex isotherm). If the trace analyte

elutes before the overloaded component, the trace analyte will be *displaced* to a shorter retention time and sharpened by the sharp front edge of the overloaded peak [22,35]. If the trace analyte is more strongly retained than the overloaded component, the trace analyte is partially eluted by the overloaded component, resulting in the trace analyte peak being broadened and eluting earlier than if the overload peak was not present. This is known as the *tag-along* effect [12,22,28,35].

Second, if the isotherm is concave, overload causes fronting peaks [8,12,35]. If the trace analyte elutes after the overloaded component, the trace analyte will experience *retainment* to a longer retention time due to the sharp back edge of the overloaded peak [28]. The trace component peak also becomes more sharpened. If the trace analyte is less retained than the overloaded component, the trace component peak becomes broadened and is smeared into the more retained, severely fronting overloaded peak [15,28,35]. An additional requirement for fronting to occur is that the additive or eluent must be deficient in the region of the overloaded peak [10,36]. For this to occur, the overloaded solute peak must displace the additive resulting in combined elution and the excess of the additive eluting before the solute followed by a negative additive peak gradient [10]. It is the deficiency in the eluent that results in the increase broadening. Thus, in this *pull-back* effect, the extent of this smearing is dependent on the concentration of the overloaded component and the concentration of the eluent [35].

The above behaviors have been studied for classical convex and concave isotherms. However, overload in IC is due to a competitive Langmuir isotherm behavior [8]. It is not known how overload under such conditions will impact nearby trace peaks. We will use the impact of overloaded chloride on bromate under typical IC conditions to study the effect of overload under competitive Langmuir isotherm conditions.

## 3. Experimental

### 3.1. Materials and chemicals

All chemicals were of analytical (ACS) grade. Sodium bromate (>99.0%) was from Sigma-Aldrich (St. Louis, MO, USA). Sodium chloride (99.0%) was from EMD Chemicals (Gibbstown, NJ, USA), and anhydrous sodium sulfate anhydrous ( $\geq 99.0\%$ ) from Fisher Scientific (Morristown, NJ, USA). Deionized water (>17.9 M $\Omega$ -cm) from a Thermo Scientific Barnstead E-Pure water generator (Marrieta, OH, USA) was used for the preparation of standards and other solutions. For the overload studies, the concentration of bromate was kept at 10 mM and the concentration of chloride varied from 10 to 300 mM. Duplicate runs were performed on three columns (IonPac AS9-HC, AS19 and AS23, Thermo Scientific, Sunnyvale, CA, USA) detailed in Table 1 for the hydroxide, carbonate and carbonate/bicarbonate eluents. The dead time was determined from the water dip (or positive peak, under overload conditions).

### 3.2. Instrumentation

All analyses were performed on a Thermo Scientific ICS-2000 ion chromatography system equipped with a conductivity detector. Tubing connections between the IC system components were PEEK. Thermo Scientific Dionex EGC III NaOH and EGC III K<sub>2</sub>CO<sub>3</sub> eluent generator cartridges were used to produce high purity hydroxide, carbonate and bicarbonate eluents. For the carbonate and carbonate/bicarbonate eluent systems, an EGC carbonate mixer was installed between the eluent degasser and the injection valve. The eluent flow rate was 1 mL/min for all the runs. Samples were injected using a 20  $\mu\text{L}$  PEEK loop. All injections were done randomly and in duplicate. All columns (Table 1) were 4  $\times$  250 mm

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