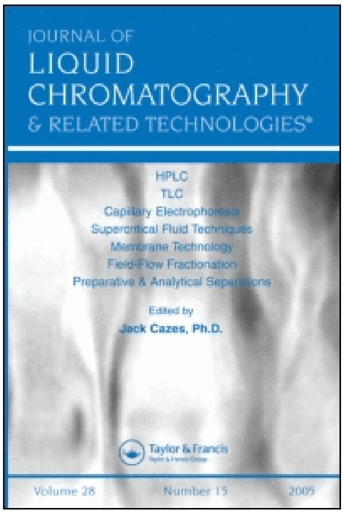

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Linearity in Ion Chromatography

Lee N. Polite[a]; Harold M. Mcnair[a]; Roy D. Rocklin[b]
[a] Department of Chemistry, Virginia Polytechnic Institute & State University, Blacksburg, Virginia [b] Dionex Corporation Sunnyvale, California

To cite this Article Polite, Lee N. , Mcnair, Harold M. and Rocklin, Roy D.(1987) 'Linearity in Ion Chromatography', Journal of Liquid Chromatography & Related Technologies, 10: 5, 829 — 838
To link to this Article: DOI: 10.1080/01483918708066738
URL: http://dx.doi.org/10.1080/01483918708066738

JOURNAL OF LIQUID CHROMATOGRAPHY, 10(5), 829-838 (1987)

LINEARITY IN ION CHROMATOGRAPHY

Lee N. Polite[1], Harold M. McNair[1], and
Roy D. Rocklin[2]*
[1]*Department of Chemistry*
Virginia Polytechnic Institute & State University
Blacksburg, Virginia 24061
[2]*Dionex Corporation*
Sunnyvale, California 94088-3603

ABSTRACT

Using ion chromatography with chemical eluant suppression, peak heights and peak areas are determined for the anions chloride and sulfate and the cations sodium and potassium in standard solutions. Calibration curves are prepared for the ions and shown to be linear over the tested range, nearly five orders of magnitude.

INTRODUCTION

Ion chromatography (IC) is a powerful and versatile analytical tool. Using ion exchange separation, a large number of both inorganic and organic anions and cations can be separated. In the most commonly used configuration, electrical conductivity detection is used with chemical eluant suppression. The original IC configuration was introduced in 1975 by Small, Stevens, and Bauman (1) and used low capacity pellicular ion exchange separator columns followed by high capacity packed bed suppressors of the opposite type as the separator. Since that time, there have been major improvements in both separator and suppressor technology. Today, high efficiency five and ten micron resins are used for both isocratic and gradient elution to separate a large number of ions in one chromatographic run. Continuously regenerated membrane suppressors with low internal volumes have replaced packed bed suppressors, eliminating the problems of peak broadening and the need for periodic suppressor regeneration (2).

Ion chromatography is now used to analyze a wide range of sample types, with analyte ion concentrations ranging from sub parts-per-billion to per-cent levels. Quantitative analysis is usually accomplished by preparing a multi-level calibration curve from the peak heights or peak areas of known standards and comparing the response of the analytes in the sample to the standard curve. Although the best-fit line through the calibration points is usually linear, a curve calculated from a quadratic equation should be used in the event of deviation from linearity. The calculation of a best-fit curve from a quadratic equation can be tedious, and is best performed by computer. However, when computing equipment is not available and a strip chart recorder is used, linear calibration curves are used. A common practice in ion chromatography employing chemical eluant suppression when many analyses must be performed in a short time is the use of a single calibration point, with the line drawn through the origin. It is obvious that in this case, accurate quantitative analysis will not result if the detector response is not linear.

Several studies have been performed on linearity in ion chromatography, including studies by Pohl and Johnson (3) and by Doury-Berthod et al (4). In the latter report, complex equations are derived demonstrating that peak height response in anion exchange chromatography with suppressed conductivity detection is not linear. This prediction is in conflict with our experience and with the results presented by Pohl and Johnson, and in this paper, we report results from calibration curves prepared for several anions and cations.

EXPERIMENTAL

All experiments were performed on a Dionex Model 4010i ion chromatograph. This system consists of a high-pressure pump, a chromatography module to contain the injection valve and the column and suppressor, and a conductivity detector. Conditions for the chromatography are as follows:

Anion determinations

Separator: HPIC-AS4A
Eluant: 0.75 mM $NaHCO_3$, 2.2 mM Na_2CO_3
Suppressor: Anion MicroMembrane (AMMS)
Regenerant: 25 mN H_2SO_4

Cation determinations

Separator: HPIC-CS3
Eluant: 12 mM HCl, 0.5 mM diaminopropionic acid, monohydrochloride
Suppressor: Cation MicroMembrane (CMMS)
Regenerant: 50 mM tetrabutylammonium hydroxide

For both anion and cation determinations, the flow rates were 1.0 mL/min, and the sample loop volume was 50 µL. Calibration curves were generated from the minimum detection limit up to 1,000 parts-per-million.

RESULTS AND DISCUSSION

Due to the extreme range of concentrations used to produce the calibration curves, plots of log (peak height or area) vs. log (concentration) were used. For log/log calibration plots, a slope of one will result from linear calibration curves of arithmetic plots, i.e. direct plots of peak height or area vs. analyte concentration. Log/log slopes of greater than one indicate upward curvature on arithmetic plots, and log/log slopes of less than one indicate downward curvature. Calibration curves for sodium and chloride are shown in figures 1 and 2. The slopes and correlation coefficients from these plots, as well as from plots for potassium and sulfate, are listed in table 1.

Calibration slopes from peak area are 0.99 for sodium and potassium and 1.01 for chloride. For each of these ions, the peak area calibration slopes are closer to one than the peak height plots. Correlation coefficients are also closer to one for the peak area plots. Both the slope and correlation coffecient results indicate that peak area determinations produce a better linear fit than peak height. For sulfate, the peak height slope is 1.00 and the peak area slope is 1.03. The correlation coefficients are roughly the same. As can be seen in figures 1 and 2, both peak area and peak height plots are linear up to several hundred

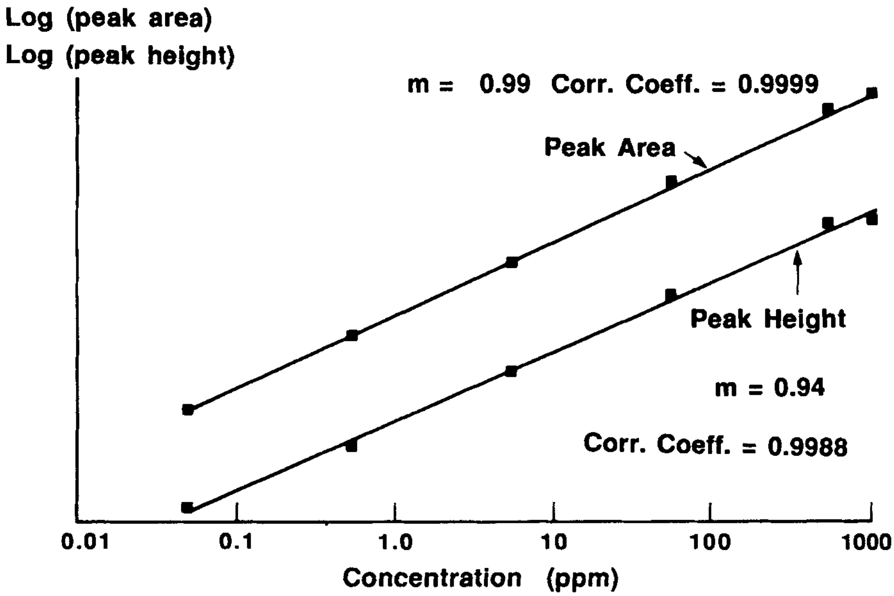

Figure 1. Quantitation of sodium by area and height.

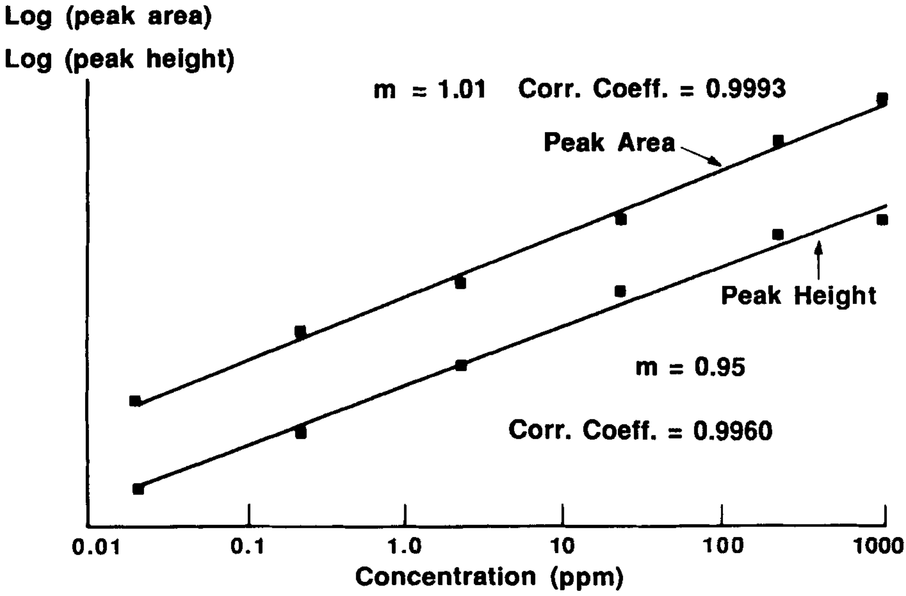

Figure 2. Quantitation of chloride by area and height.

TABLE I.

Comparison of calibration curves from peak area and height

ION	METHOD	SLOPE	CORRELATION COEFF.
Sodium	Area	0.99	0.9999
Sodium	Height	0.94	0.9988
Potassium	Area	0.99	0.9999
Potassium	Height	0.85	0.9970
Chloride	Area	1.01	0.9993
Chloride	Height	0.95	0.9960
Sulfate	Area	1.03	0.9992
Sulfate	Height	1.00	0.9991

ppm. At higher concentrations, the ratio of peak height to area decreases as column overload broadens the peak. This produces a downward curvature in the peak height calibration plot. When calibration plots indicate column overload, samples should be diluted or smaller injection volumes used. If column overload can not be avoided, peak area should be used for quantitative analyses.

The results presented here are in conflict with the theoretical plots generated by Doury-Berthod et al (4), who predict non-linear calibration curves. Their explanation for this prediction is as follows: There are two factors that determine the conductivity change during elution. The first is the increase in conductivity caused by the elution of analyte ions. The second is the decrease in conductivity caused by the decrease in eluant ion concentration during the elution of analyte ions. This is called the vacancy peak. When the eluant consists of a carbonate, bicarbonate buffer, the conductivity change during the vacancy peak should be dependent on analyte concentration in a non-linear manner. Since the pK_a of carbonic acid is 6.37, there is some dissociation following suppression of the resulting carbonic acid, producing a significant background conductivity. The deviation from linearity predicted by Doury-Berthod should be caused by the effect of the increasing hydrogen ion concentration during the elution of the strong acid analytes suppressing the ionization of carbonic acid. The extent of this ionization suppression is dependant on the analyte ion's concentration. The sum of the conductivity changes from these factors should produce a non-linear calibration curve.

For the determination of cations, there should be very little deviation from linearity as the eluant largely consists of the strong acid HCl. The cation eluant is suppressed almost to zero background, so vacancy peaks following suppression are extremely small in comparison to the contribution of the analytes.

The main reason for our different results for anion calibration curves is probably caused by the use of different suppressors and by different eluant concentrations. The total carbonate concentration used by Doury-Berthod was 5 mM. The total carbonate concentration in the eluant we used for the HPIC-AS4A anion separator is 2.95 mM. The lower eluant concentration should minimize the effect of the vacancy peak, resulting in a more linear calibration curve. Also, Doury-Berthod used a packed suppressor, we used a continuously regenerated membrane suppressor. We have observed that the Anion MicroMembrane Suppressor (AMMS) produces background conductivities approximately 10% lower than those obtained with packed bed suppressors.

This decreased background conductivity is caused by several factors. First, it is possible that some carbonic acid can convert to carbon dioxide and water, and diffuse through the membrane to the regenerant solution, thus lowering the background conductivity. This could not occur in a packed bed suppressor. Second, the membrane suppressor might not be as efficient in removing sodium as the packed bed suppressor. Since the equivalent conductance of sodium is considerably lower than that of hydrogen, a small amount of sodium reaching the detector would result in lower background conductivity. (A 10% decrease in background conductivity for the anion eluant would result from a suppression efficiency of 99.8%.) This effect is observed for packed bed suppressors immediately prior to suppressor exaustion, as the baseline first dips slightly just before increasing off scale. Third, during operation of the AMMS, a very small amount of sulfuric acid regenerant leaks through the membrane and reaches the detector cell. (Sulfate in the suppressor effluant has been detected by re-injecting the effluant.) This is of course not a problem for quantitative analysis, as the leakage occurs after separation, and can not add or subtract from peaks. The leakage of sulfuric acid should suppress the ionization of carbonic acid, thus limiting the effect of the elution of the strong acid anions. While sulfuric acid leakage should cause an increase in background conductivity, it is possible that all three of the factors listed here may be occuring, with the net conductivity change being negative.

When all of the factors listed above are considered, it is apparent that many simplifying assumptions must be made in order to derive an equation for conductivity. Whether or not an equation can be developed that accurately predicts the observed results, the important conclusion from the data presented here is that when ion chromatography is performed with membrane suppressors and calibration curves are prepared from peak areas, the curves are linear over a very wide range of analyte concentrations. In the case of the ions tested, the linear range is from the minimum detection limit, measured in parts-per-billion, to above 0.1%. This is a range of nearly five orders of magnitude.

A direct solution to the question of linearity is to use sodium hydroxide as the eluant since it is converted to water following suppression, so there can be no effect from the vacancy peak. Membrane suppressors can suppress the high concentrations of sodium hydroxide required to elute polyvalent ions.

The analytical range of ion chromatography can easily be extended beyond the range reported here. More concentrated samples can be diluted so that the analyte concentrations will be within the linear range. For example, Rocklin used ion chromatography to determine per-cent level concentrations of ions in mixed acid etching solutions (5). For trace analyses, analyte ions can be concentrated on short ion exchange columns by pumping the sample over the concentrator column. This method was introduced in a paper by Wetzel at al in 1979 (6). In a recent report by Houskova and Chu (7), concentration techniques were used to determine anions in deionized water. Minimum detection limits were reported as low as 50 parts-per-trillion.

Depending on analyte concentrations, samples can be analyzed using either preconcentration, direct injection, or dilution followed by direct injection. With the use of these techniques, the analytical range of ion chromatography can extend from 50 parts-per-trillion to 50%, a range of ten orders of magnitude.

REFERENCES

1. Small, H.; Stevens, T.S.; and Bauman, W.C., *Anal. Chem.* **47** (1975), 1801
2. Stillian, J. *L.C. Mag.* **4** (1985), 802
3. Pohl, C.A. and Johnson, E.L. *J. Chromatographic Sci.* **18** (1980), 442-452
4. Doury-Berthod, M.; Giampaoli, P.; Pitsch, H.; Sella, C.; and Poitrenaud, C., *Anal. Chem.* **57** (1985), 2257-2263
5. Rocklin, R.D., *Semiconductor Int.* May, 1986
6. Wetzel, R.; Anderson, C.; Schleicher, H.; Crook, G. *Anal. Chem.* **51** (1979), 1532
7. Houskova, J.; Chu, T. *Solid State Tech.* May, 1986, 205