

# Performance of poly(vinyl alcohol) gel columns on the ion chromatographic determination of perchlorate in fertilizers†

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*Received 8th October 2001, Accepted 6th November 2001*

*First published as an Advance Article on the web 12th December 2001*

Interest in possible sources of perchlorate ( $\text{ClO}_4^-$ ) that could lead to environmental release has been heightened since the Environmental Protection Agency placed this anion on its Contaminant Candidate List for drinking water. Although recent investigations have suggested that fertilizers are minor contributors to environmental perchlorate contamination overall, there is still interest in screening commercial products for possible contamination and quantitating perchlorate when it is found. Ion chromatography (IC) has been used for this application owing to its speed, low detection limits, widespread availability, and moderate ruggedness relative to other techniques. However, fertilizer matrixes complicate the IC analysis relative to potable water matrixes. In this study, the performance of poly(vinyl alcohol) gel resin IC columns (100 mm and 150 mm) was evaluated for fertilizer matrixes using method EPA/600/R-01/026. The NaOH eluent included an organic salt, sodium 4-cyanophenoxide. Detection was by suppressed conductivity. A set of 55 different field samples representing 48 products and previously used by the EPA to assess occurrence of perchlorate in fertilizers (EPA/600/R-01/049) was reanalyzed on the 150 mm column. The 100 mm column was used to further investigate the positive hits. Both columns gave satisfactory performance in fertilizer matrixes, with spike recoveries ( $\pm 15\%$ ), assured reporting levels ( $0.5\text{--}225 \mu\text{g g}^{-1}$  except for one at  $1000 \mu\text{g g}^{-1}$ ), accuracy (relative error  $< 30\%$  always and most  $< 15\%$ ), and precision [injection-to-injection reproducibility  $< 3\%$  relative standard deviation (RSD)] comparable to those reported in other studies. Performance did not vary substantially between column lengths. Lastly, the results of this investigation provided further evidence in support of the conclusions that had been reached previously by the EPA on the occurrence of perchlorate in fertilizers.

## Aim of investigation

Besides its association with defense and aerospace activities, perchlorate ( $\text{ClO}_4^-$ ) is a known contaminant in some fertilizers, in particular, natural saltpeters, in which perchlorate is present as a native impurity. It is found as a component of caliche (sodium nitrate-bearing ores) mined in South America, especially in Chile, and its formation is speculated to occur *via* meteorological processes.<sup>1–3</sup> Mined caliche is refined, the insoluble matter is discarded, and the resulting product is sold as sodium nitrate fertilizer (16-0-0). It may also be used to manufacture fertilizer grade potassium nitrate (14-0-0) as well as blends of the two salts. Awareness of the presence of perchlorate in some fertilizers has increased since 1999,<sup>4–12</sup> and led the Environmental Protection Agency (EPA) to investigate its occurrence in a multitude of commercial fertilizers recently.<sup>13</sup> Perchlorate has been found in surface waterways and underground aquifers in several U.S. states, and is generally associated with point sources, such as military installations and aerospace industrial sites.<sup>14–17</sup> Because of its potential impact on thyroid function,<sup>18</sup> the EPA's Office of Ground Water and Drinking Water added perchlorate to the Contaminant Candidate List (CCL) for drinking water in 1998.<sup>19</sup>

Ion chromatography (IC) has been the principal technique employed to test environmental samples for perchlorate,<sup>20</sup> and it is the basis of methods for drinking waters<sup>21</sup> and fertilizers.<sup>22</sup> Previous applications of IC to fertilizers have relied on columns that could be used to effectively separate perchlorate without an organic additive, such as 4-cyanophenoxide, which is a polarizable anion of low charge density and can therefore displace perchlorate from the resin. In fact, in a recent comparison of laboratory performance on fertilizer analysis conducted by the EPA, all participating laboratories indicated they had used such columns.<sup>23</sup> The high ionic strength typical of fertilizer matrixes complicates the analyses and raises IC detection limits relative to drinking water or standards made in deionized water.<sup>23</sup> In this report, we examine the performance of poly(vinyl alcohol) (PVA) gel columns on fertilizer matrixes and compare the results to those obtained previously.<sup>23</sup> Unlike previous fertilizer work, the eluent here contained 4-cyanophenoxide, which is prepared *in situ* by the addition of 4-cyanophenol to a solution of sodium hydroxide. In part, our objective was to determine if such an approach, which was equivalent to initial approaches to drinking water, could be readily applied to the fertilizer matrices. PVA columns have been used to analyze potable, waste, and ground water samples with performance comparable to that of other columns on the market,<sup>24</sup> but have not been tested on the kinds of solutions that typically result from dissolving or leaching fertilizers. Such solutions have dissolved matter concentrations and ionic strengths that are characteristically much higher than raw or

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finished drinking water. Although all IC columns suffer from reduced performance as ionic strength is increased, this effect was pronounced in a study which relied on 4-cyanophenoxide anion to displace sorbed perchlorate ion.<sup>25</sup> Consequently, matrix interference could potentially limit the applicability of columns where organic modifiers are required for analysis of fertilizers.

## Experimental section

### Fertilizer samples

The processes used for the selection and collection of field samples and the subsequent reduction to laboratory samples have been described previously.<sup>13,23</sup> Portions of archived materials were shipped under tamper-evident custody seal to the Metrohm-Peak laboratory by overnight courier. A combination of agricultural and horticultural fertilizers and additives were investigated, including urea, ammonium phosphates, calcium phosphates, sodium nitrate, potassium nitrate, ammonium nitrate, potassium chloride, and potassium magnesium sulfate, among others, as well as commercially formulated admixtures thereof. All of the field samples were solids. The samples represented by the individual entries in Table 1 were provided to the analyst with unique, randomly assigned 5-digit identifiers and only general descriptions of the chemical composition to minimize introducing bias on the part of the analyst.

### Sample treatment

House distilled water was polished with a Milli-Q system (Millipore, Milford, MA, USA) to achieve a resistivity of at least 18 MΩ cm; this water was used throughout. For samples containing a nitrate salt (NaNO<sub>3</sub>, KNO<sub>3</sub>, NH<sub>4</sub>NO<sub>3</sub>, or a mixture thereof) as the only major constituent, a 100 g mass

was combined with 1.0 L of Milli-Q water, except for sample 55b for which there was insufficient quantity. Sample 55b was a homogenized material and prepared the same as the other products. For all other materials, 4.00 ± 0.05 g portions were weighed out and combined with 40.0 ± 0.5 mL of Milli-Q water to give a fertilizer mass to water volume ratio of 10 g dL<sup>-1</sup>, or ~10% w/w. The soluble solids were dissolved by shaking overnight (~12–15 h) on a wrist-action shaker. This allows sufficient time for leaching soluble salts from the insoluble matter present in many products at significant levels. The liquids were decanted into 15 mL centrifuge tubes and spun for 20–30 min at 3600 rpm on an International Equipment Co. (Needham Heights, MA, USA) HN-SII centrifuge. When turbidity was still visually observable, the centrifugates were filtered through 0.45 μm poly(vinylidene difluoride) syringe filters; only some centrifugates required filtration.

### Ion chromatography

The ion chromatograph consisted of a modular system (Metrohm Ltd., Herisau, Switzerland) equipped with a 709 pump, 732 conductivity detector, 762 software interface, 753 suppressor, 766 autosampler, and 733 separation center. A guard column was not employed, but an RP disc (inline filter) was placed at the head of the column and replaced when either pressure increases or discoloration was observed. The separation center enclosure included a six-port injection valve fitted with a sample loop, a conductivity detector cell, a micro-capillary packed bed suppressor, and an analytical column. The chemical suppressor operates from a three-port switching valve that allows the use of a freshly regenerated suppressor prior to each chromatographic analysis, *i.e.*, prior to each injection. The chemical suppressor is continually regenerated with an aqueous solution containing 0.10 M H<sub>2</sub>SO<sub>4</sub> and 0.10 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. In these experiments, oxalic acid was added to the

**Table 1** Sample identification<sup>a</sup>

| Sample | Description <sup>b</sup>  | Sample <sup>c</sup> | Description  | Sample | Description  |
|--------|---|---------------------|--|--------|--|
| 1      | TRF 22-3-14   | 21                  | ag K <sub>2</sub> SO <sub>4</sub>                    | 38     | ag GTSP <sup>e</sup>   |
| 2      | ag (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>               | 22                  | ag (NH <sub>4</sub> )SO <sub>4</sub>                 | 39     | ag (NH <sub>4</sub> )H <sub>2</sub> PO <sub>4</sub>  |
| 3      | ag urea   | 23                  | ag (NH <sub>4</sub> )H <sub>2</sub> PO <sub>4</sub>  | 40     | ag (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>  |
| 4      | ag KCl  | 24                  | ag iron oxide  | 41     | ag limestone   |
| 5      | ag iron oxide   | 25                  | ag limestone   | 42     | ag KNO <sub>3</sub> <sup>d</sup>   |
| 6      | ag limestone  | 26                  | ag urea  | 43     | TRF 10-10-10   |
| 7      | ag K <sub>2</sub> Mg <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> | 27                  | ag clay  | 44     | Clay   |
| 8      | ag KCl  | 28                  | ag KCl   | 45     | ag K <sub>2</sub> Mg <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>                              |
| 9      | TRF 18-6-12   | 29                  | ag urea  | 46     | ag KNO <sub>3</sub>  |
| 10     | TRF 36-6-6  | 30                  | ag NH <sub>4</sub> NO <sub>3</sub>                   | 47     | ag (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>  |
| 11     | SPF 20-20-20  | 31a                 | ag (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>  | 48a    | ag GTSP <sup>e</sup>   |
| 12     | ag K <sub>2</sub> Mg <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> | 31b                 | ag (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>  | 48b    | ag GTSP <sup>e</sup>   |
| 13     | ag K <sub>2</sub> Mg <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> | 32                  | ag (NH <sub>4</sub> )H <sub>2</sub> PO <sub>4</sub>  | 49     | ACSR KCl + 6.8 mg g <sup>-1</sup> ClO <sub>4</sub> <sup>-</sup> (K <sup>+</sup> ) <sup>f</sup> |
| 14     | ag K <sub>2</sub> Mg <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> | 33a                 | ag KNO <sub>3</sub> + NaNO <sub>3</sub> <sup>d</sup> | 50     | SPF + 6.2 mg g <sup>-1</sup> ClO <sub>4</sub> <sup>-</sup> (Na <sup>+</sup> ) <sup>f</sup>     |
| 15     | ag limestone  | 33b                 | ag KNO <sub>3</sub> + NaNO <sub>3</sub> <sup>d</sup> | 51     | ag GTSP + 2.7 mg g <sup>-1</sup> ClO <sub>4</sub> <sup>-</sup> (Na <sup>+</sup> ) <sup>f</sup> |
| 16     | ag (NH <sub>4</sub> )SO <sub>4</sub>                              | 34a                 | ag NH <sub>4</sub> NO <sub>3</sub>                   | 52     | ag urea + 1.8 mg g <sup>-1</sup> ClO <sub>4</sub> <sup>-</sup> (NH <sub>4</sub> ) <sup>f</sup> |
| 17     | ag urea   | 34b                 | ag NH <sub>4</sub> NO <sub>3</sub>                   | 53     | ag KCl <sup>f</sup>  |
| 18     | ag (NH <sub>4</sub> )SO <sub>4</sub>                              | 35                  | ag KNO <sub>3</sub> <sup>d</sup>                     | 54     | ag NH <sub>4</sub> NO <sub>3</sub> <sup>f</sup>  |
| 19     | ag (NH <sub>4</sub> )H <sub>2</sub> PO <sub>4</sub>               | 36                  | ag NaNO <sub>3</sub> <sup>d</sup>                    | 55a    | ag NaNO <sub>3</sub> <sup>d,f</sup>  |
| 20     | ag K <sub>2</sub> Mg <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> | 37                  | ag NH <sub>4</sub> NO <sub>3</sub>                   | 55b    | ag NaNO <sub>3</sub> <sup>d,f</sup>  |

<sup>a</sup>Detailed manufacturer/supplier and site data are presented in ref. 23. <sup>b</sup>The designation “ag” refers to an agricultural grade commodity chemical; these grades often contain impurities or additives not found in reagent grade chemicals. The designation “ACSR” refers to an American Chemical Society reagent grade chemical. SPF = water-soluble plant food; TRF = timed-release fertilizer (*e.g.*, a lawn winterizer). The hyphenated numbers are the guaranteed analyses (N:P:K ratios), where the macronutrients are expressed as follows: nitrogen as N, phosphorus as P<sub>2</sub>O<sub>5</sub>, and potassium as K<sub>2</sub>O. <sup>c</sup>For samples 31, 33, 34, 48, and 55, the letter notation (a or b) identifies blind duplicate solid samples from which distinct test solutions were prepared and analyzed by IC. <sup>d</sup>These samples are derived from caliche; therefore, perchlorate is expected as a naturally occurring impurity. Typical perchlorate concentrations encountered in recent manufacturing lots have varied from 1 to 2 mg g<sup>-1</sup>, but steps have been taken to reduce the concentrations by 90–95%. For further detail, see refs. 1 and 13. <sup>e</sup>Granular triple superphosphate (GTSP) is a somewhat ill-defined mixture of hydrated calcium phosphates. It contains primarily calcium dihydrogenphosphate monohydrate, Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, but species with other degrees of protonation and hydration may also be found as part of the admixture. In pure form, GTSP should normally have a guaranteed analysis of 0.46–0. <sup>f</sup>These items were supplied as quality control standards. They were prepared and evaluated by the EPA. The cation listed in parentheses indicates the perchlorate salt used to fortify the material, if any. The native materials were verified to be perchlorate-free within the limits of experimental error by the EPA prior to fortification. No analyte was added to samples 53, 54, or 55. However, sample 55 is a caliche-derived material and contains perchlorate naturally at a concentration of 1.7 mg g<sup>-1</sup>.

suppressor regenerant to complex any residual metal cations left behind by the samples.

Metrosep A Supp 5 (4 × 100 mm and 4 × 150 mm) columns (Metrohm Ltd.) with an average resin particle diameter of 5 µm were used throughout this study. All samples were subjected to analysis on the 150 mm column, while the 100 mm analytical column was reserved for further exploration and comparison of those samples that were already found to contain perchlorate using the 150 mm column. Sample loop sizes were 500 µL for the 100 mm column, and 1000 µL for the 150 mm column. The eluent was ~17–20 mM NaOH with sodium 4-cyanophenoxide (prepared *in situ*) used as a modifier at a concentration of 1 mM for the 100 mm column or 2.5 mM for the 150 mm column. The exact NaOH concentration was unimportant because the perchlorate peak was well resolved from other peaks and any shifts in retention time were discernible based on the behavior of an analyte-fortified sample. The eluent flow rate was 0.70 mL min<sup>-1</sup> regardless of column length. Column lifetime is about 9–12 months with heavy use, that is, several days a week of nonstop running during which strong base is in constant contact with the resin.

### Eluent

All solutions were prepared with reagent grade chemicals dissolved in Milli-Q water. Sodium hydroxide (50% w/w, J.T. Baker, Phillipsburg, NJ, USA) and 4-cyanophenol (95% purity, Aldrich, Milwaukee, WI, USA) were used to prepare the eluent. A volume of 1.05 mL of 50% w/w NaOH(aq) was combined with a mass of 4-cyanophenol (0.119 g for 1.0 mM or 0.298 g for 2.5 mM) in a polypropylene bottle and diluted to 1.0 L with deionized water. This resulted in a post-mixing eluent NaOH concentration of 20 mM (neglecting the reaction with the 4-cyanophenol) and the 4-cyanophenoxide concentrations specified above. In fact, the acid–base reaction was non-negligible; accordingly, neutralization of the phenolic organic modifier reduced the eluent NaOH concentration by 1.0 mM or 2.5 mM. The resulting solutions were degassed under vacuum and stored under Ascarite II<sup>®</sup> (EM Science, Gibbstown, NJ, USA) to protect against CO<sub>2</sub> contamination.

### Perchlorate standard

A 1.00 g L<sup>-1</sup> stock solution of sodium perchlorate (99% purity, Sigma, St. Louis, MO, USA) was prepared by dissolving 1.23 g

of the solid and diluting to 1.00 L with deionized water. This stock solution was used to prepare all working standards throughout these experiments *via* serial dilutions.

## Results and discussion

### Column and instrument performance

Calibrations using standards made in Milli-Q water were done on both columns. Two sets of calibration data were acquired. A low-level (labeled “ppb” in Table 2) calibration was done using eight concentrations ranging from 2.06 to 206 ng mL<sup>-1</sup> with each solution injected in duplicate. A high level (labeled “ppm”) calibration was done using six concentrations ranging from 0.206 to 9.99 µg mL<sup>-1</sup> with each solution injected in duplicate. Calibration results are given in Table 2. Each set of data was fitted to a linear function using an unweighted least squares regression, as is common practice in IC.

There is attenuation of the response in moving from the ppb calibration to the ppm calibration. Specifically, we would expect the slopes for the ppm calibrations to be about 1000-fold the slopes of the ppb calibrations based simply on the analyte concentrations. However, the ratio of the slopes of the 150 mm column is 16, and the ratio of the slopes of the 100 mm column is 5.6. While all of the regression coefficients are greater than 0.99, there is clearly nonlinear variation in sensitivity, as indicated by the change in slope; therefore, careful calibration is required over the concentration range of interest. When the calibration region is large enough that deviations from linearity become apparent, as is the case here, an unweighted least squares regression sacrifices the quality of the fit for data nearer to the origin (where the ordinate values are smaller in magnitude) and necessitates multiple calibration intervals. This is most conspicuous when examining the ppm calibration. The data for the low-concentration standards essentially become irrelevant in an unweighted fit. The *y*-intercepts for both columns are statistically indistinct from zero, *i.e.*, their uncertainties are larger than their magnitudes. Nevertheless, that alone is not sufficient proof of the goodness of fit, for the magnitude of both the *y*-intercept (which incidentally is negative) and its standard error are such that no concentration below 0.7 ppm can be quantitated using the regression line found from these standards. This is evident from the back-calculated analyte concentrations (identified as [ClO<sub>4</sub><sup>-</sup>]<sub>calc</sub> in Table 2) found using either the *y*-intercept or its error. We

**Table 2** Calibration results

| Parameter <sup>a</sup>   | ppb calibration |            | ppm calibration |             |
|--|-----------------|------------|-----------------|-------------|
|  | 100 mm          | 150 mm     | 100 mm          | 150 mm      |
| $m \pm \varepsilon_m^d$  | 44.3 ± 0.07     | 52.8 ± 0.2 | 252 ± 7         | 848 ± 27    |
| $\varepsilon_m/m$ (%)  | 0.15            | 0.34       | 2.81            | 3.18        |
| $b \pm \varepsilon_b$ (unitless)   | -38 ± 18        | -18 ± 48   | -256 ± 400      | -565 ± 1525 |
| $\varepsilon_b/b$ (%)  | -46             | -268       | -156            | -270        |
| $R^2$  | 0.99997         | 0.9998     | 0.992           | 0.990       |
| $1 -  b/\varepsilon_b $  | -1.18           | —          | —               | —           |
| $ b /A_{5ppb}$ (ppb) <sup>b</sup> or $ b /A_{0.5ppm}$ (ppm) (%)                      | 20              | 7.3        | 74              | 18          |
| $ b /A_{10ppb}$ (ppb) <sup>b</sup> or $ b /A_{1ppm}$ (ppm) (%)                       | 9.5             | 3.6        | 30              | 8.0         |
| $\varepsilon_b/A_{10ppb}$ (ppb) <sup>b</sup> or $\varepsilon_b/A_{1ppm}$ (ppm) (%)   | 4.4             | 9.7        | 47              | 12          |
| $\varepsilon_b/A_{100ppb}$ (ppb) <sup>b</sup> or $\varepsilon_b/A_{10ppm}$ (ppm) (%) | 0.42            | 0.94       | 3.4             | 1.0         |
| [ClO <sub>4</sub> <sup>-</sup> ] <sub>calc</sub> for $b^c$                           | -0.86           | -0.33      | -1.01           | -0.67       |
| [ClO <sub>4</sub> <sup>-</sup> ] <sub>calc</sub> for $ b  + \varepsilon_b^c$         | 1.26            | 1.23       | 2.61            | 2.47        |

<sup>a</sup>Key:  $m$  = slope,  $\varepsilon_m$  = standard error in slope,  $\varepsilon_m/m$  = relative error in slope;  $b$  = *y*-intercept,  $\varepsilon_b$  = standard error in *y*-intercept,  $\varepsilon_b/b$  = relative error in *y*-intercept;  $A$  = a peak area for the concentration indicated by the subscript. <sup>b</sup>The notation (ppb) or (ppm) refers to the columns of data to which the parameter applies, columns 2 and 3 or columns 4 and 5, respectively. <sup>c</sup>[ClO<sub>4</sub><sup>-</sup>]<sub>calc</sub> is the back-calculated value of the analyte concentration assuming a peak area equal to either the *y*-intercept ( $[ClO_4^-]_{calc} = b/m$ ) or the sum of the *y*-intercept and its standard error ( $[ClO_4^-]_{calc} = (|b| + \varepsilon_b)/m$ ) as indicated in the entry. This is an artefactual detection limit based on the calibration standards; see text for further explanation. It is negative when the *y*-intercept is negative, and its absolute value represents a measure of an artefactual method detection limit resulting from the choice of calibration standards. Units for this parameter are (ng mL<sup>-1</sup>) for columns 2 and 3 and (µg mL<sup>-1</sup>) for columns 4 and 5. <sup>d</sup>Units for the slope are reciprocal concentration units, *i.e.*, (mL ng<sup>-1</sup>) for columns 2 and 3 and (mL µg<sup>-1</sup>) for columns 4 and 5.



emphasize that this behavior is a result of the concentrations chosen for the calibration standards and therefore is related to these calibration curves rather than the columns specifically. It does not mean that the columns and instrument are incapable of measuring concentrations below these values, but that the specific calibration lines under discussion cannot be used. These artefactual limits of detection can be improved by increasing the number of points chosen at low concentration, by weighting those points, by restricting the concentration domain, and/or by fitting the data to a nonlinear function. At some point, the systematic variation in sensitivity (*i.e.*, net instrument/detector nonlinearity) is no longer a governing factor, and the indeterminate error in the measurement controls the value obtained for the detection limit.

Similarly, we can compare the peak areas of the lowest standards with the magnitudes of the *y*-intercepts and their standard errors. This comparison is especially telling for the ppb calibrations. For the 100 mm column, the *y*-intercept is equal to 20% of the area of a 5.00 ng mL<sup>-1</sup> standard. On the other hand, for the 150 mm column, the *y*-intercept is equal to only 7.3% of the area of a 5.00 ng mL<sup>-1</sup> standard. At first glance, this suggests that the detection limits should be lower on the 150 mm column. Nevertheless, we must also consider the standard errors of the *y*-intercepts. The trend in ratios ( $\epsilon_b/A_{5\text{ppb}}$ ) of the standard errors of the *y*-intercepts to the areas of the 5 ppb standards is reversed; that is, the 100 mm column has a ratio of 0.42 (better), while the 150 mm column has a ratio of 0.94 (worse). The larger this ratio, the closer the standard error is in magnitude to the area of the lowest standard. Other similar ratios are also provided in Table 2 for comparison. Furthermore, the back-calculated concentrations,  $[\text{ClO}_4^-]_{\text{calc}}$ , allow the contrast to be seen straightforwardly. In this fashion, performance near the detection limit is concluded to be more-or-less the same for both column lengths.

As explained above, performance exceeding the artefactual detection limits induced by the calibration curves is attainable. For example, if a 3.00 ng mL<sup>-1</sup> standard is injected eight times, a method detection limit (MDL) may be calculated as described.<sup>13</sup> At the 99% confidence level, it is determined as follows:  $\text{MDL} = t_{0.01,7} \times \sigma_{n-1} \times [3.00 \text{ ng mL}^{-1}]/A_{\text{av}}$ , where  $t_{0.01,7} = 2.998$  (the value of Student's *t* for seven degrees of freedom at the 99% confidence level),  $\sigma_{n-1}$  = the standard deviation of the eight replicate peak areas, and  $A_{\text{av}}$  = the average of the eight replicate peak areas. For the 100 mm column, the MDL was 0.48 ng mL<sup>-1</sup> ( $A_{\text{av}} = 106.8$ ,  $\sigma_{n-1} = 5.8 \text{ ng mL}^{-1}$ ,  $\text{RSD} = 5.4\%$ ); for the 150 mm column, the MDL was 0.35 ng mL<sup>-1</sup> ( $A_{\text{av}} = 149.3$ ,  $\sigma_{n-1} = 5.9 \text{ ng mL}^{-1}$ ,

$\text{RSD} = 4.0\%$ ). If the MDL is used as the criterion of performance, the 150 mm column outperformed the 100 mm column just slightly since the 100 mm column has an MDL 38% larger than that of the 150 mm column. Ten consecutive injections of a 5.00 ng mL<sup>-1</sup> standard gave an MDL of 0.16 ng mL<sup>-1</sup>; when repeated the next day, an MDL of 0.18 ng mL<sup>-1</sup> was obtained (150 mm column;  $t_{0.01,9} = 1.383$ ).

### Accuracy

Consistent with previous findings,<sup>13,23</sup> perchlorate was found only in those materials either (i) into which it had been deliberately added (*i.e.*, a quality control sample), or (ii) known to be derived from Chilean caliche and contain perchlorate as a consequence. The relative difference between the measured concentrations obtained with the 150 mm column used in this study and those obtained in a previous EPA study ranged from -8.2 to +2.1% as indicated in Table 3. As has been observed previously,<sup>23</sup> there was a negative bias in the results. It is not clear whether that bias is systematic or merely a trend in the indeterminate error. Performance was better when the matrix consisted of sodium nitrate or urea rather than potassium chloride, and that was also consistent with previous investigations. In terms of the utility of the method and column for screening products for the presence of perchlorate, the performance is satisfactory and comparable with that obtained previously.<sup>23</sup>

### Precision

Intrarun (*i.e.*, within a sequence of consecutive injections) injection-to-injection reproducibility was good; RSDs for triplicate injections were within 2.9% at the most. With ten consecutive injections, RSDs were 2.3% for a 5.00 ng mL<sup>-1</sup> standard and 2.8% for a 10.0 ng mL<sup>-1</sup> standard on the 150 mm column. When repeated the next day, the RSDs were 2.6% for a 5.00 ng mL<sup>-1</sup> standard and 2.9% for a 10.0 ng mL<sup>-1</sup> standard. In general, injection-to-injection RSDs were less than 1%, as shown in Table 3. This was somewhat better than the aggregate performance obtained previously;<sup>23</sup> however, such a comparison is not entirely fair since the uncertainties in that study were expressed as a measure of interlaboratory—rather than intralaboratory—variation. For the two blind duplicates, the precision was very good. On the 100 mm column, the two values (obtained as averages of triplicate injections) differed by -1.9% for sample 33 and +2.1% for sample 55. On the 150 mm column, the two values (also obtained as averages of triplicate injections) differed by 0.073% for sample 33 and 4.2%

**Table 3** Perchlorate concentrations and relative differences found in fertilizer samples resulting from different columns

| Sample <sup>a</sup> | Grav concn/<br>μg g <sup>-1b</sup> | 100 mm PVA<br>column concn/<br>μg g <sup>-1c</sup> | 150 mm PVA<br>column concn/<br>μg g <sup>-1c</sup> | Relative difference<br>in concn for 100 mm vs.<br>150 mm column <sup>d</sup> (%) | EPA study average<br>concn/μg g <sup>-1c,e</sup> | Relative difference<br>in concn for EPA<br>study vs. 150 mm <sup>f</sup> (%) |
|---------------------|------------------------------------|--|--|--|--|--|
| 33a                 | —                                  | 4209 ± 2   | 4113 ± 4   | -2.33%   | 3970 ± 190                                       | -3.6   |
| 33b                 | —                                  | 4130 ± 7   | 4116 ± 13  | -0.34%   | 3980 ± 230                                       | -3.5   |
| 35                  | —                                  | 2288 ± 19  | 2277 ± 11  | -0.48%   | 2330 ± 200                                       | +2.1   |
| 36                  | —                                  | 1946 ± 15  | 1937 ± 6   | -0.46%   | 1920 ± 100                                       | -1.0   |
| 42                  | —                                  | 2408 ± 5   | 2438 ± 4   | 1.23%  | 2480 ± 250                                       | +1.5   |
| 49                  | 6800                               | 5802 ± 15  | 6138 ± 12  | 5.47%  | 6080 ± 250                                       | -0.96  |
| 50                  | 6200                               | 5575 ± 15  | 5881 ± 12  | 5.20%  | 5440 ± 300                                       | -8.2   |
| 51                  | 2700                               | 2119 ± 61  | 2388 ± 25  | 11.26%   | 2400 ± 240                                       | +0.51  |
| 52                  | 1800                               | 1671 ± 4   | 1600 ± 5   | -4.44%   | 1620 ± 170                                       | +1.0   |
| 55a                 | 1700                               | 1676 ± 1   | 1587 ± 4   | -5.61%   | 1590 ± 100                                       | +0.19  |
| 55b                 | 1700                               | 1712 ± 3   | 1657 ± 1   | -3.32%   | —  | —  |

<sup>a</sup>The letter notation (a or b) is used to delineate duplicate solid samples. These were not identified to the laboratory as the same exact material. Distinct test solutions were prepared and injected into the IC. <sup>b</sup>The gravimetric value is calculated from the known formulation; known masses of a perchlorate salt and a fertilizer (which essentially serves as a diluent) were combined in the EPA laboratory as reported in ref. 23. <sup>c</sup>Reported uncertainty is the estimated standard deviation for three replicate injections of the same test solution. <sup>d</sup>Relative difference =  $(C_{150\text{mm}} - C_{100\text{mm}})/C_{150\text{mm}} \times 100\%$ . <sup>e</sup>Values were taken from Table 4 in ref. 23. A duplicate of sample 55 was not included in the previous EPA study. <sup>f</sup>Relative difference is computed for the concentrations obtained using the 150 mm Metrosep A Supp 5 column *versus* the average from the EPA study; relative difference =  $(C_{\text{EPA}} - C_{150\text{mm}})/C_{\text{EPA}} \times 100\%$ .

for sample 55. When the solution for solid sample 33 (which contained  $4114 \mu\text{g g}^{-1}$ ) was injected 10 times in succession, the estimated standard deviations for the solid material were  $6.6 \mu\text{g g}^{-1}$  one day and  $16 \mu\text{g g}^{-1}$  the following day, which give respective RSDs of 0.16% and 0.39% (150 mm column).

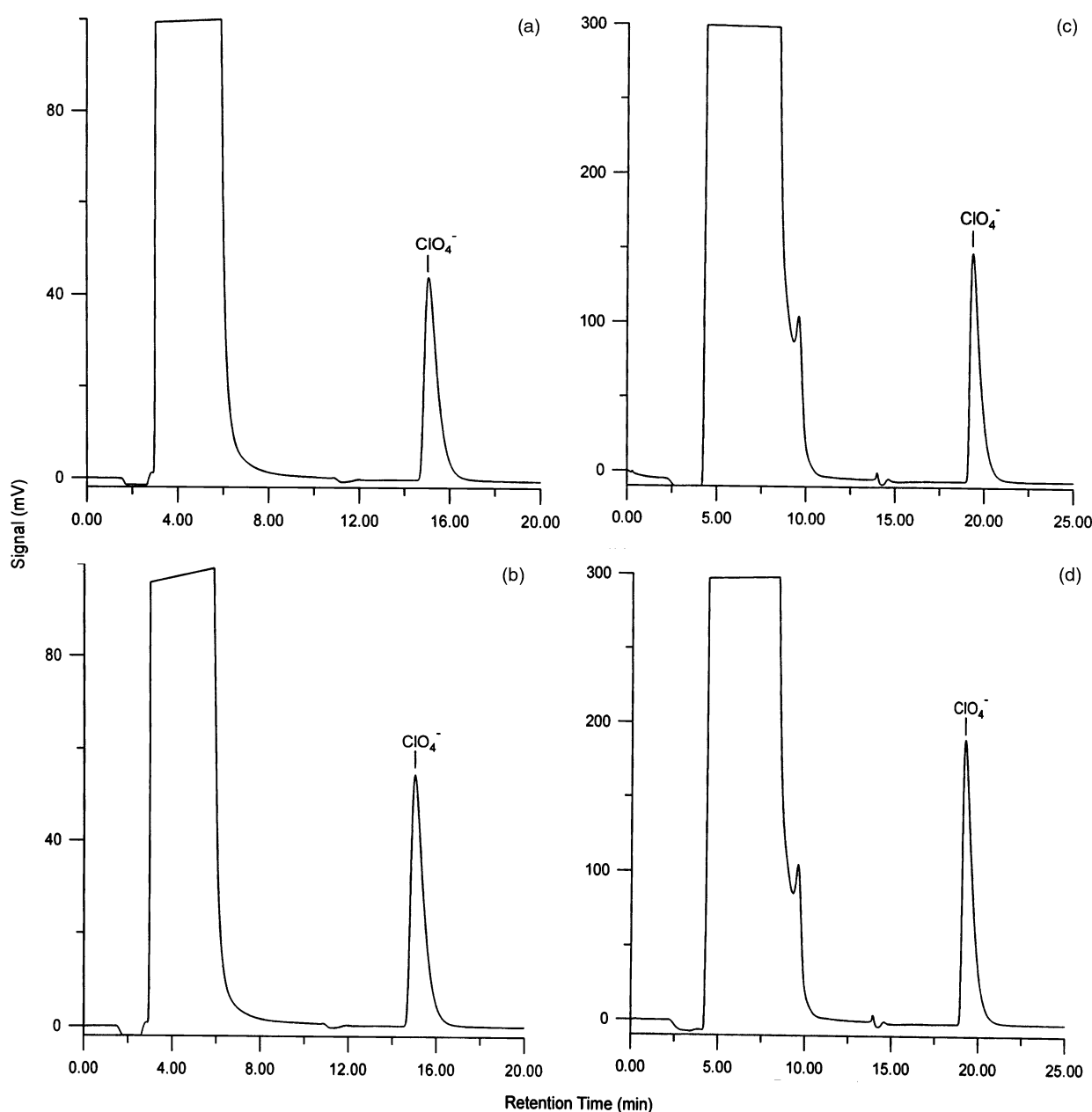
Interrun (day-to-day) variation on the 150 mm column was larger than intrarun variation. The average peak area based on 10 injections fell by 5.6% for a  $5.00 \text{ ng mL}^{-1}$  standard and 7.6% for a  $10.0 \text{ ng mL}^{-1}$  standard from one day to the next. Similarly, the average peak area based on 10 injections of the solution derived from sample 33 fell by 4.7% from one day to the next. Of course, this level of variation is within the  $\pm 20\%$  limit imposed by EPA/600/R-01/026, but can be eliminated by recalibration.

There was a statistically significant difference in the concentrations measured using the 100 mm column as opposed to the 150 mm column. No clear bias was observable when comparing the data obtained using the different columns; sometimes the concentrations were higher on one column and sometimes on the other. The relative differences between the

concentrations measured on the two columns (value from 150 mm column as compared with that from 100 mm) varied from a minimum (in magnitude) of  $-0.34\%$  (sample 33b) to a maximum of 11.3% (sample 51). In comparing the relative differences on the blind duplicates, there is satisfactory precision. For sample 33, it was  $-2.3\%$  for sample 33a *versus*  $-0.34\%$  for sample 33b. For sample 55, it was  $-5.6\%$  for sample 55a *versus*  $-3.3\%$  for sample 55b. Overall, this suggests that performance is consistent.

### Recovery of fortifications

For those materials in which perchlorate was detected, the recoveries of all injections of 20% spikes (*i.e.*, spikes equal to 20% of the measured analyte concentrations in the injected solutions) were in the range 93.6–104.7% for the 100 mm column and 91.9–103.7% for the 150 mm column. Resolution of the analyte peak, and the increase in size upon fortification are illustrated in Fig. 1 for a caliche-based sodium nitrate fertilizer. The average recoveries (based on duplicate injections)



**Fig. 1** Ion chromatograms of Chilean sodium nitrate fertilizer (sample 55a) prepared at  $2.0 \text{ mg mL}^{-1}$  ( $1/100$  dilution of  $10 \text{ g dL}^{-1}$ ) on Metrosep A Supp 5 columns; (a and b) on 100 mm column using  $500 \mu\text{L}$  loop: (a) unspiked, showing native perchlorate peak, (b) the same solution as in (a) plus a 20% spike; (c and d) on 150 mm column using  $1000 \mu\text{L}$  loop: (c) unspiked, showing native perchlorate peak, (d) the same solution as in (c) plus a 20% spike.

**Table 4** Spike<sup>a</sup> recoveries in perchlorate-containing samples

| Sample | 100 mm column (%) |           | 150 mm column (%) |           |
|--------|-------------------|-----------|-------------------|-----------|
|        | 20% spike         | 50% spike | 20% spike         | 50% spike |
| 33a    | 102.6             | 105.2     | 101.8             | 102.8     |
| 33b    | 102.5             | 104.0     | 102.3             | 103.3     |
| 35     | 100.7             | 103.0     | 101.5             | 100.8     |
| 36     | 100.9             | 102.6     | 101.8             | 101.8     |
| 42     | 100.7             | 103.5     | 100.7             | 102.0     |
| 49     | 102.5             | 105.1     | 100.8             | 103.4     |
| 50     | 101.6             | 100.8     | 97.9              | 102.1     |
| 51     | 97.9              | 100.1     | 101.7             | 104.4     |
| 52     | 101.5             | 101.9     | 100.3             | 99.3      |
| 55a    | 101.1             | 102.9     | 98.6              | 102.1     |
| 55b    | 102.7             | 105.3     | 100.7             | 102.9     |

<sup>a</sup>The term 20% spike refers to a fortification equal to 20% of the analyte concentration found in the injected solution so that the post-fortification analyte concentration is 1.2 times the original concentration measured in the solution. Likewise, the term 50% spike refers to a fortification equal to 50% of the analyte concentration found in an injected solution so that the post-fortification analyte concentration is 1.5 times the original concentration measured in the solution.

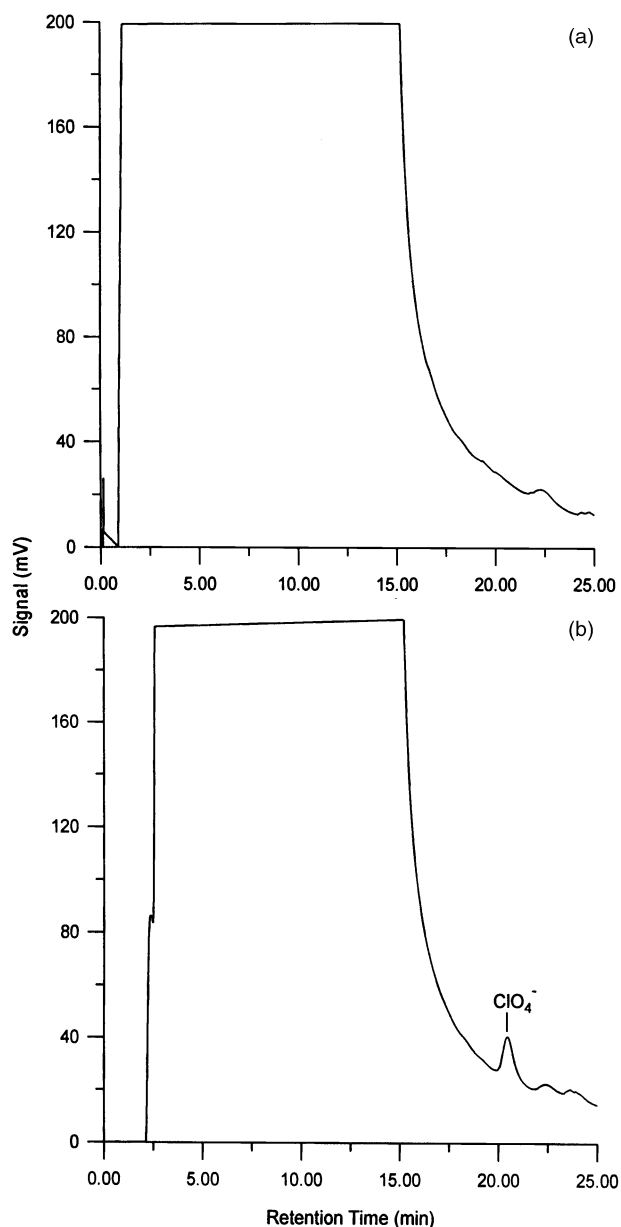
of 20% spikes and 50% spikes for solutions derived from perchlorate-containing materials are reported in Table 4 for both columns. Response remains linear in this region as shown by the excellent recoveries, which are well within the  $\pm 20\%$  interval required by the method.<sup>22</sup> For those materials in which perchlorate was undetectable, the recovery of a  $10 \text{ ng mL}^{-1}$  spike was 81.0–111.8% for all individual runs using the 150 mm column; these solutions were not run using the 100 mm column. Average recoveries (based on duplicate injections) are reported in Table 4. Even at this low concentration (*i.e.*,  $10 \text{ ng mL}^{-1}$ ), Fig. 2 shows that the perchlorate peak is readily distinguished from the baseline and matrix background signal.

### Preliminary assured reporting levels

The preliminary assured reporting level (pARL) is a matrix-specific detection limit based on the satisfactory recovery of a fortification and the dilution required to reach that recovery.<sup>13,22,23</sup> In the case of a material for which no peak corresponding to perchlorate could be distinguished from the baseline noise, the recovery of a  $10.0 \text{ ng mL}^{-1}$  spike was used to determine the pARL. For the materials in which perchlorate was undetectable, the pARLs ranged from 0.5 to  $1000 \mu\text{g g}^{-1}$  and are given in Table 5. The pARLs for duplicates sometimes varied due to limitations posed by time, quantity of sample, or other operating resources. The most striking difference was for sample 48, where the  $10^{-3}$  dilution yielded 93.4% recovery of the spike ( $\text{pARL} = 100 \mu\text{g g}^{-1}$ ), and the  $10^{-4}$  dilution yielded 84.6% recovery of the spike ( $\text{pARL} = 1000 \mu\text{g g}^{-1}$ ). Since EPA/600/R-01/026 requires a recovery of 80–120%, this represents a close case, and the factor of 10 between the reported pARLs should not be viewed as an inconsistency in the data. In fact, if this single pARL at  $1000 \mu\text{g g}^{-1}$  were to be excluded, the next highest value would be  $225 \mu\text{g g}^{-1}$ . Other perchlorate-free duplicates gave pARLs as follows: sample 31 ( $10 \text{ versus } 45 \mu\text{g g}^{-1}$ ) and sample 34 (both  $5.0 \mu\text{g g}^{-1}$ ). The pARLs compared favorably with, and were often better than, those obtained in the EPA's prior investigation.<sup>23</sup> Due to the large number of samples tested and the time involved in rigorously determining a true ARL, further investigation was deemed unnecessary.

### Conclusion

When used with a soluble 4-cyanophenoxide salt as an additive in the NaOH eluent, PVA columns (100 and 150 mm) are satisfactory in separating perchlorate from other anions found



**Fig. 2** Ion chromatograms of 22-3-14 lawn fertilizer (sample 1) prepared at  $5.0 \text{ mg mL}^{-1}$  ( $1/20$  dilution of  $10 \text{ g dL}^{-1}$ ) on a 150 mm Metrosep A Supp 5 column: (a) no perchlorate peak is discernible in the original solution, (b) solution in (a) fortified with  $10 \text{ ng mL}^{-1}$  of the analyte.

in common fertilizer products despite high ionic strength and dissolved matter, allowing analyte detection and quantitation by suppressed conductivity. The columns are sufficiently robust in these matrices to allow them to be used for EPA/600/R-01/026, a method for screening fertilizers for perchlorate. Performance on fortified samples and quality control standards, assured reporting levels, and precision are comparable to columns used in other investigations. Moreover, data obtained in this study corroborate the perchlorate concentrations reported for agricultural and horticultural products examined by the EPA to assess occurrence of perchlorate in fertilizers and related products.

### Acknowledgements

This work was collaboration between the EPA and Metrohm-Peak, Inc. It has been subjected to agency review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation

**Table 5** Spike (10 ng mL<sup>-1</sup>) recoveries and preliminary assured reporting levels (pARL) in perchlorate-free samples (150 mm column)

| Sample | Dilution factor <sup>a</sup> | Recovery (%) | pARL/ $\mu\text{g g}^{-1}$ | Sample | Dilution factor | Recovery (%) | pARL/ $\mu\text{g g}^{-1}$ |
|--------|------------------------------|--------------|----------------------------|--------|-----------------|--------------|----------------------------|
| 1      | 20                           | 100.4        | 2                          | 26     | 20              | 98.9         | 2                          |
| 2      | 500                          | 103.7        | 50                         | 27     | 10              | 101.4        | 1                          |
| 3      | 20                           | 96.1         | 2                          | 28     | 50              | 99.0         | 5                          |
| 4      | 50                           | 94.5         | 5                          | 29     | 10              | 95.2         | 1                          |
| 5      | 100                          | 103.7        | 10                         | 30     | 50              | 99.3         | 5                          |
| 6      | 5                            | 93.9         | 0.5                        | 31a    | 100             | 94.3         | 10                         |
| 7      | 20                           | 99.7         | 2                          | 31b    | 450             | 100.4        | 45                         |
| 8      | 50                           | 95.2         | 5                          | 32     | 470             | 92.6         | 47                         |
| 9      | 470                          | 103.3        | 47                         | 34a    | 50              | 96.7         | 5                          |
| 10     | 470                          | 103.8        | 47                         | 34b    | 50              | 96.9         | 5                          |
| 11     | 970                          | 94.1         | 97                         | 37     | 50              | 99.5         | 5                          |
| 12     | 20                           | 103.1        | 2                          | 38     | 1000            | 94.5         | 100                        |
| 13     | 20                           | 91.8         | 2                          | 39     | 450             | 96.5         | 45                         |
| 14     | 20                           | 98.0         | 2                          | 40     | 100             | 97.1         | 10                         |
| 15     | 10                           | 98.5         | 1                          | 41     | 5               | 97.3         | 0.5                        |
| 16     | 50                           | 96.0         | 5                          | 43     | 450             | 101.0        | 45                         |
| 17     | 10                           | 98.1         | 1                          | 44     | 10              | 107.8        | 1                          |
| 18     | 100                          | 95.6         | 10                         | 45     | 20              | 100.9        | 2                          |
| 19     | 20                           | 93.8         | 2                          | 46     | 50              | 99.7         | 5                          |
| 20     | 20                           | 97.5         | 2                          | 47     | 420             | 95.9         | 42                         |
| 21     | 2250                         | 95.3         | 225                        | 48a    | 10000           | 84.6         | 1000                       |
| 22     | 50                           | 95.8         | 5                          | 48b    | 1000            | 93.4         | 100                        |
| 23     | 450                          | 101.8        | 45                         | 53     | 50              | 97.0         | 5                          |
| 24     | 100                          | 102.7        | 10                         | 54     | 50              | 103.7        | 5                          |
| 25     | 10                           | 98.0         | 1                          |        |                 |              |                            |

<sup>a</sup>Dilution factor refers to the subsequent volumetric dilution of 1 part of a 10 g dL<sup>-1</sup> leachate or solution to the number of parts listed in the table prior to injection on the IC.

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