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Control of errors in anion chromatography applied to environmental research

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Abstract

Chemically suppressed ion chromatography has developed into a precise and reliable method for quantifying common anionic species. Equipment has improved, columns have been developed to offer faster analysis and three generations of chemical suppressors have evolved to provide easier care and improved performance. A range of sample types which include rainwater, soil solutions and canopy leachates have been analysed. A build-up of sample impurities gradually affects the performance of the column resulting in loss of separation and increase in mobile phase back-pressure over time. Approximately 8000 samples per annum have been analysed for chloride, nitrate and sulphate over a period of 11 years. A quality system describing calibration characteristics, measures of accuracy, precision and a model for quality control are presented.

1. Introduction

At Merlewood Research Station ion chromatography is employed routinely for the analysis of chloride, nitrate and sulphate in environmental samples. This technique is used in conjunction with inductively coupled plasma-optical emission spectrometry (ICP-OES) for cation analyses and continuous flow colorimetry for ammonium, phosphate, silicate and dissolved organic carbon to provide an analytical facility for ecological researchers. The laboratory has had 11 years experience in anion analysis using ion chromatography. During this period separator columns have improved and a new type of membrane suppressor has been developed. Ion chromatography provides a very reliable and robust analytical technique.

The Analytical Section routinely analyses rainfall, cloud water, throughfall/canopy leachates, soil solutions and stream/drainage water. Samples typically originate from projects studying nutrient cycling in forest or moorland ecosystems or monitoring pollutant movement. Throughput is in the region of 8000 aqueous samples per annum from sites and experimental plots distributed throughout the UK. Typically, samplings occur at fortnightly or monthly intervals, with researchers collecting and preparing samples for submission to the analytical laboratory. This experimental approach requires clear protocols in the field and the laboratory, as well as rigorous quality control (qc) procedures for analytical methods.

A variety of texts exist [1–3] providing general advice on types of quality control procedures with rare publications reporting the application of quality systems [4,5]. Mullins [3] proposed a working model for detecting bias from internal quality control. Within this model the fundamen-

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tal problem is to establish a σ value for each determination which provides a realistic estimate of the spread of results. Miller's [6] statement that "the practical question is clear: should outlying results be rejected or not before the mean, standard deviation etc. of the data are calculated" focuses on the major issue facing laboratories who attempt to use "real" data-sets to establish working control limits.

The objective of this paper is to evaluate the components of the methodology needed to produce good quality data from chemically suppressed anion chromatography. It includes consideration of calibration procedures, column degradation and common interferences encountered in the analysis of mainly aqueous samples. The whole quality system is also reviewed. A method for quality control in water analysis using synthetic reference samples is proposed. Options for determining working limits for internal quality control, the use of control charts and the benefits of regular participation in a national proficiency testing scheme are discussed.

2. Experimental

2.1. Sample preparation

Samples are collected from the field site, filtered through GF/F filter within 24 h, stored at 4°C and analysed as soon as possible, usually within 4 weeks of collection. Immediately prior to ion chromatography, all samples are filtered through a glass fibre and a membrane filter (< 0.45 μm) and passed through a C_{18} cartridge to remove possible organic contaminants. To minimise sample processing cost, filters are used for a batch of (up to 25) samples or until difficulty is experienced in passing the solution through the filter. Filters are cleaned with 30 ml water between each sample to eliminate possible cross contamination of samples.

2.2. Equipment

Dionex 2010i ion chromatograph is used with a conductivity detector, auto sampler (ISCO) and sample load pump. A PC data system (AI450) is used to control automation through contact closures and to change ranges on the detector to optimise the performance for each ion (range settings $Cl^- = 300$ μS cm^{-1}, $NO_3^- = 10$ μS cm^{-1} and $SO_4^{2-} = 100$ μS cm^{-1}). A procedure has been established to wash each side of the 4-way injection valve between samples to prevent sample carry-over.

2.3. Column

The system is configured with AG4A guard and AS4A separator columns and operated with a mobile phase of $NaHCO_3$ (2.8 mM) and Na_2CO_3 (2.2 mM) at a flow-rate of 1.8 ml min^{-1}. k' Values are calculated from the relative separation of F^- (t_1) and SO_4^{2-} (t_2) [$k' = (t_2 - t_1)/t_1$]. A micro membrane chemical suppressor (0.0125 M H_2SO_4 flow-rate = 3 ml min^{-1}) reduces the background conductivity from the mobile phase.

2.4. Analytical run

The instrument is calibrated daily with 8 standards (prepared fresh each week) followed by an analytical run of 99 samples. There are drift check samples every 11 experimental samples and qc samples with each batch of samples (maximum of 25). Data is transferred from the chromatography software (.csv file) into the laboratory management system for report compilation.

2.5. Quality control samples

Synthetic solutions (Table 1) for use as quality control reference samples are analysed with each batch. Analytical data from these samples is used to verify that the analytical process is under control. It has been established that: each stock solution is stable for one year; separate synthetic reference solutions are needed for cation checks; working solutions are prepared on the day of analysis by accurate dilution of the stock solution (one hundred-fold); synthetic solutions are also

Table 1
Recipe for anion solution (stock reference 3)

Chemical	Weight (g)	Theoretical solution concentration (mg l^{-1})
NH_4Cl	0.382	15 Cl
NaCl	2.05	
$NaNO_3$	0.607	1.0 NO_3-N
Na_2SO_4	1.059	2.5 SO_4^{2-}-S
Na_2SiF_6	0.671	1.0 Si
Na_2HPO_4	0.0687	0.15 PO_4^{3-}-P

Dissolve salts separately in water, combine and dilute to one litre.

stable at half concentration (Ref. [4]); a minimum of 2 qc samples need to be analysed with each batch of environmental samples to produce useful qc information.

2.6. Computation of standard deviation (σ) from quality control samples to derive warning and action limits for Shewhart charts

σ can be calculated by three alternative methods: (1) using the full data-set; (2) a computation based on the spread of the results within the inter-quartile range (IQR) i.e., sort data, determine median, divide data into quartiles, determine quartile range on quartiles adjacent to median (IQR); $\sigma_{(IQR)} = IQR/1.35$; (3) a computation of the median value of all the differences from the median; median of absolute deviation (MAD) = median $[|x_i - \text{median}(x_i)|]$; $\sigma_{(MAD)} = MAD/0.6745$.

2.7. Quality control model

Mullins [3] proposed the following model to evaluate quality control measurements: (1) one reading outside 3 standard deviations (σ); (2) nine points in a row on one side of the mean; (3) six points in succession increasing or decreasing; (4) fourteen points in a row alternating up and down; (5) two out of three points outside 2σ; (6) four out of five points in sequence greater than σ; (7) fifteen points in a row within plus or minus σ; (8) eight points in a row beyond σ (above or below).

In practice, we have found points 1, 2 and 5 the most useful indicators.

3. Results and discussion

3.1. Anion chromatography performance

Ions of interest

Ion chromatography is routinely used for the analysis of aqueous samples for Cl^-, NO_3^-, SO_4^{2-}. Sample phosphate-P concentrations in natural ecosystems tend to be low (0.005–0.2 mg l^{-1}), therefore they are more difficult to analyse under standard chromatographic conditions. In order to quantify low levels of P down to 0.005 mg l^{-1}, PO_4^{3-} analysis is more conveniently determined on a multi-channel continuous flow colorimetry system (molybdenum blue).

Calibration

Studies over a period of 10 years have repeatedly shown that there were significantly lower residuals when a 3rd order regression was applied to calibration data (Table 2). The same effect applied for the hollow fibre suppressor originally used and, more recently, to the replacement micro-membrane suppressor. The initial impression gained, on the evaluation of the correlation coefficient (r) (Table 2), is that the data fit is linear. Further examination of the correlation values (r^2) confirms that the relationship is best described by a 3rd order mathematical equation.

Duory-Berthod et al. [7] predicted deviation from linearity caused by the effect of the increasing hydrogen ion concentration during elution of the strong acid analytes as they suppressed the ionisation of carbonic acid. Polite et al. [8] investigated the chloride linearity of calibration with a micro-membrane suppressor over 5 orders of magnitude and reported linear calibration with a correlation coefficient of 0.9960. Chloride analysis over the calibration range 0.1 to 25 mg l^{-1} can yield a bias in the region of 5% (mid-

Table 2
Calibration data (May 1994)

Cl^- (mg l^{-1})	Cl^- area	NO_3^--N (mg l^{-1})	NO_3^--N area	SO_4^{2-}-S (mg l^{-1})	SO_4^{2-}-S area
0	4.4	0	0	0	82.4
2.5	147.0	0.3	403.4	1.0	360.9
5	326.6	0.6	734.5	2.0	687.5
7.5	427.7	0.9	1116	3.0	1036
10	602.4	1.2	1568	4.0	1449
15	904.9	1.8	2367	6.0	2235
20	1278	2.4	3220	8.0	3069
25	1671	3.0	4363	10	4072

Correlation coefficients from calibration data

Coefficient	Order of fit	Cl^-	NO_3^-	SO_4^{2-}
r		0.9979	0.9974	0.9973
r^2	1st	0.9957	0.9951	0.9946
r^2	2nd	0.9992	0.9991	0.9998
r^2	3rd	0.9994	0.9996	0.9998
Cl^-	$y = 6.32 + 59.6x - 0.281x^2 + 0.0225x^3$			
NO_3^-	$y = -4.39 + 1330x - 98.0x^2 + 46.4x^3$			
SO_4^{2-}	$y = 67.7 + 296x + 10.4x^2 - 0.00997x^3$			

range) for a linear calibration when compared to a 3rd order calibration prediction.

Care is required if laboratories adopt a policy of using computer 3rd order predictions for evaluating calibration response. False values may occur when samples exceed the value of the top calibration response by a factor of 2 (e.g., cloud water sometimes exceed concentrations of 50 mg l^{-1} Cl^-). Checking procedures need to be devised to monitor both the area and solution concentration in order to detect samples requiring dilution and re-analysis.

Contamination of columns by components from the sample matrix

The guard column, connected into the chromatography system, provides an effective and vital function in protecting the separator column. Soluble organic compounds or other soluble components of the sample, such as trace metals, present in samples collected for environmental studies gradually accumulate on the guard column. This deterioration in the column produces loss in separation efficiency in the system and poses a threat to the separator column. Soil solution from the organic horizon and stem flow from coniferous trees can have a significant impact (Table 3) on the guard column within a short period (e.g. 10 samples). In contrast, soil solution from mineral soil horizons, throughfall and rainfall do not contain sufficient contaminants to produce deterioration on the guard column.

Table 3
Effects of sample matrices on guard column efficiency (n = 10)

Solution matrix	k' Factor	Change detected
Rain	1.84	+0.03
Mineral soil solution	1.83	−0.01
Organic soil solution	1.68	**−0.15**
Throughfall	1.65	−0.03
Stem flow	1.48	**−0.18**

With use, the separation efficiency k' of the guard column is gradually reduced whilst there is also an associated increase in column back-pressure (Fig. 1). The manufacturers recommend columns should be cleaned or replaced when k' reaches half its original value. Leaks begin to occur, most notably in the load/inject valve, when the combined back-pressure of the guard and separator column exceeds 1400 p.s.i. (1 p.s.i. = $6.89 \cdot 10^3$ Pa). Guard columns are discarded when the combination of reduced separating efficiency and high back pressure results in unacceptable chromatographic performance which could lead to contamination of the analytical column. Sodium nitrate has been found to be the most effective salt for cleaning out contaminants from guard columns; note the improvements in performance at events 4, 10 and 17 (Fig. 1) after guard column clean-up.

Stationary phase cartridges provide a means of removing substances which contribute to deterioration in the guard column and in the performance of the chromatographic system. SEP-PAK C_{18} solid-phase extraction cartridges (Waters) absorb some of the organic content; 33 and 45% of the dissolved organic carbon, respectively, was removed from throughfall and from organic horizon soil solution. It is our policy to remove some of the contaminant loading from the sample before injection. However, in economic terms, it could be argued that the guard column itself gives effective protection and should therefore be regarded as disposable.

Chromatography interferences

Samples collected from upland areas or from forest ecosystems in the UK are typically from regions of higher than average rainfall. Under these circumstances, soluble organic compounds which co-elute, such as maleate or tartrate [9] are unlikely to be present in sufficient concentrations to significantly affect the quantification of chloride, nitrate and sulphate. Soluble low molecular mass organic acids, detected in cloud water samples and aqueous extracts of plant material, elute immediately following the solvent dip and are well separated from chloride. In contrast, extracts of soil or leaf material prepared in the laboratory may require sample clean-up, changes in chromatography or integration methodology in order to quantify components accurately. For example, in a study to investigate sulphate deposition onto *Pinus sylvestris*, a chloroform pre-extraction procedure was used to remove surface waxes prior to a water extraction. Residual amounts of chloroform eluted on the leading edge of the sulphate peak so that it was impossible to quantify the peak accurately. Chloroform contamination could not be removed from the sample matrix using solid-phase clean-up (C_{18}, CN or NH2); evaporation

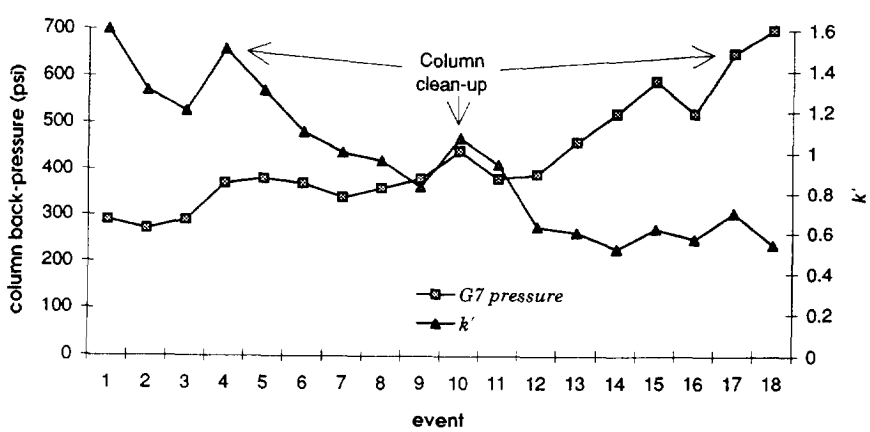

Fig. 1. Guard column back-pressure and k' over the period of analytical operation.

proved to be an effective method of contaminant removal.

3.2. Quality control for anion chromatography

Precision

Analytical laboratories gather data on the analytical performance over a period of time in order to understand the performance of the instrumental method and as a basis for establishing quality control data to validate each analysis.

Published values for within-batch precision are slightly lower than those achieved on a routine overnight analytical run (Table 4.). Within-batch data is always superior to between-batch precision. Therefore, within batch qc sample data does not provide a realistic data-set from which to derive qc limits to detect bias. It would almost certainly be too strict and would result in large numbers of valid reference sample values being flagged as outliers.

Preparation of reference samples for quality control

There is a wealth of general information on the theory and framework for quality control systems in analytical laboratories. Unfortunately most of this information relates to laboratories specialising in a few specific methods for measuring concentrations well above the detection limit for the method. For environmental water samples, the main difficulty is in obtaining a quality control reference sample which is stable and suitable for measuring bias on multi-element analysers at concentration levels within the selected calibration range.

Internal reference samples are made up from salt solutions of known theoretical composition. They are prepared completely independently of calibration stock solutions (Table 1). To maintain reference solutions with solution concentrations typical of study samples, it was necessary to prepare separate qc reference sample solutions for cation and anion analysis. To ensure that stability of the reference samples is maintained, stock solutions are prepared at 100 times the required concentration, stored in the refrigerator and diluted daily for use. Sufficient reference solution is prepared for 1.5 years, with a policy to prepare fresh stock solutions annually. The preparation of new stock solutions for each of the two reference solutions is staggered by 0.5 years to ensure continuity is maintained. These solutions are reproducible in preparation and have provided analytical data for a stable qc system over the 2.5 year review period (Fig. 2).

Use of quality control reference solutions

Two qc samples, with different anion concentrations are analysed with each batch of study samples. This protocol has provided a suitable framework for collecting information on batch bias and as a means of validating analytical data for environmental samples over a period of 8 years.

Fig. 2 illustrates nitrate quality control data for qc reference solution 3. Sub-samples of reference 3 were analysed with each batch of samples to validate the analytical values obtained within that batch of determinations. Shewhart control charts, marking the means of the two reference solutions form a working basis for detecting gross error (e.g. points in the region of batch 150).

Table 4
Within batch precision data obtained on reference 3 solution (6-7-'94) ($n = 9$)

	Chloride	Nitrate-N	Sulphate-S
Mean ($mg\,l^{-1}$)	15.9	1.16	2.90
Within batch σ	0.145	0.0101	0.0432
%R.S.D.	0.91	0.87	1.5
Within batch %R.S.D. [9]	0.7	0.7	0.5
Between batch %R.S.D. [9]	2.8	3.4	3.1

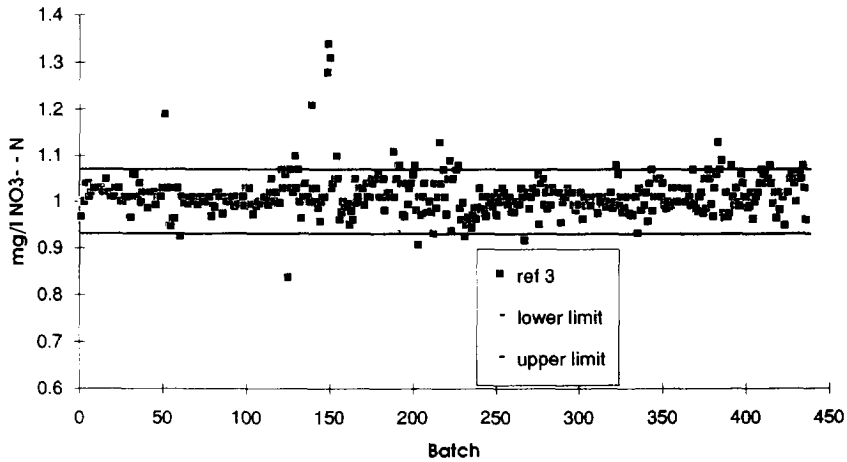

Fig. 2. Shewhart plot of NO_3^- qc reference sample 3 values obtained over a period of 2.5 years.

The plot of reference 3 NO_3^- data over a period of 2.5 years (Fig. 2) clearly shows that gross bias occurred around batch 150. Bias was confirmed by data obtained for the other qc solution analysed with those batches. It has been noted that such gross errors rarely occur and are detectable without recourse to sophisticated procedures. However, in addition to normal variation, it is evident that there are periods when the spread of data increases. This property influences the standard deviation of the data-set.

Interpretation and use of reference sample data

As discussed earlier, the main issue relates to whether any data points should be rejected from the data-set before computing standard deviation values [6].

Three general approaches are available for the treatment of outliers: parametric statistics —(Dixon or Gubbs tests) for normal distributions; non-parametric tests —inter-quartile range (IQR) and trimmed means; robust statistics —median absolute deviation (MAD).

In our experience, computation of warning and action limits at 2 and 3σ derived from the whole data-set is unlikely to provide a working system as the limits will be derived from data containing values obtained when the analytical system may have been out of control. Parametric methodology is a useful tool for rejection of one (or possibly two) outliers from a "normally distributed" population. However data-sets may be heavily tailed and skewed (Fig. 3). Non-parametric and robust statistics offer more acceptable approaches where outliers are accommodated rather than discarded and are applicable to data-sets which demonstrate non-normal distribution.

Over a short period, performance may be atypical and yield data for calculation of qc limits that are too narrow or too wide. For NO_3^- data, Table 5 shows that the analytical performance was far more precise during the first 30 determinations than during the 2.5 year period of the whole data-set, with performance over the most recent batches more typical of the whole review period. The spread of analytical data for the lower concentration reference 4 qc sample is slightly larger (0.5 mg l^{-1} NO_3^--N, 5.1% R.S.D.) compared toreference 3 (1.0 mg l NO_3^--N, 4.3% R.S.D.).

Practical significance of alternative computational methods for σ

In retrospect the qc data-set ($n = 436$) has been evaluated using a variety of basic statistical techniques and an assessment made of their application. The relative standard deviation (as %R.S.D.) computed from the median of absolute deviation (MAD) is similar to the %R.S.D. derived from the whole data-set. Ref. [4] (most recent data) is a heavily tailed distribution giving

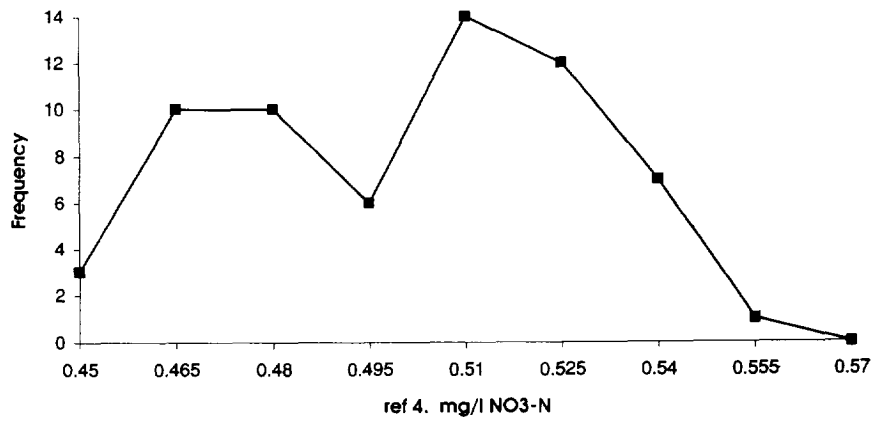

Fig. 3. Distribution histogram of recent NO_3 qc reference sample 4 data ($n = 62$).

σ calculated from MAD slightly greater than σ calculated from the whole data-set [6]. Experience has shown that limits computed on this basis includes biased data and is therefore only useful for identifying gross error and does not detect analytical bias at an early stage.

The use of the inter quartile range to determine the standard deviation provides lower values for σ than the other calculation methods. The aim of any qc system is to detect small shifts in calibration at an early stage as well as gross bias in each batch, and the use of limits based on σ derived from IQR provides a basis for detecting change either by smaller amounts or at an earlier time than with wider limits. Statistically, this is a sound approach as the IQR σ is unaffected by extreme values. However in the practical application of 3σ limits based on a single qc analysis, 12% of nitrate reference 3 values are noted as outside analytical control. Analysis of two different control samples to confirm the presence of analytical error identifies only 3% of batches as biased. Further visual evaluation of the system retrospectively confirmed that this approach was practical and provided a working basis for detecting outliers and bias at an early stage.

Quality control charts and trouble shooting

Analysts use Shewhart charts to plot qc values which contain markings to indicate the mean or median, warning and action limits. We have found that this forms the basis of a good system to identify bias or gross error when used in conjunction with a protocol for identifying the occurrence of bias (Table 5). Examination of a plot of qc data for sulphate (Fig. 4) reveals a problem between batches 250 and 300. Graphically, a plot of the cumulative sum (CUSUM) of the difference from the mean (Fig. 5), provides an alternative charting tool. Whilst Shewhart charts provide instant recognition for one rogue

Table 5
NO_3^- reference 3 qc data for relative standard deviation derived by three alternative statistical treatments

% R.S.D. (Ref. [3])	$n = 436$	$n = 30$ (first 30 from 436)	$n = 62$ (most recent data)
Whole data-set	4.3	1.9	3.8
Inter-quartile range (IQR)	1.5	1.1	1.9
Median absolute deviation (MAD)	3.0	1.9	3.4

Table 6
Comparison of recent proficiency testing data with internal qc reference values

Chloride			Nitrate			Sulphate		
%qc bias	%AQ bias	z Score	%qc bias	%AQ bias	z Score	%qc bias	%AQ bias	z Score
−2	−6	−0.33	+5	−2	−0.13	−6	−2	−0.09
+5	−5	−0.23	−4	−2	−0.11	0	−4	−0.25
+3	−2	−0.03	+3	+3	+0.16	0	−5	−0.07
0	+2	+0.06	+1	+1	+0.09	+1	−9	−0.09
+3	−4	−0.15	−3	−3	−0.14	−2	−4	−0.18
0	−5	−0.28	0	−2	−0.11	−1	0	0

AQ = AQUACHECK, Water Research Centre.

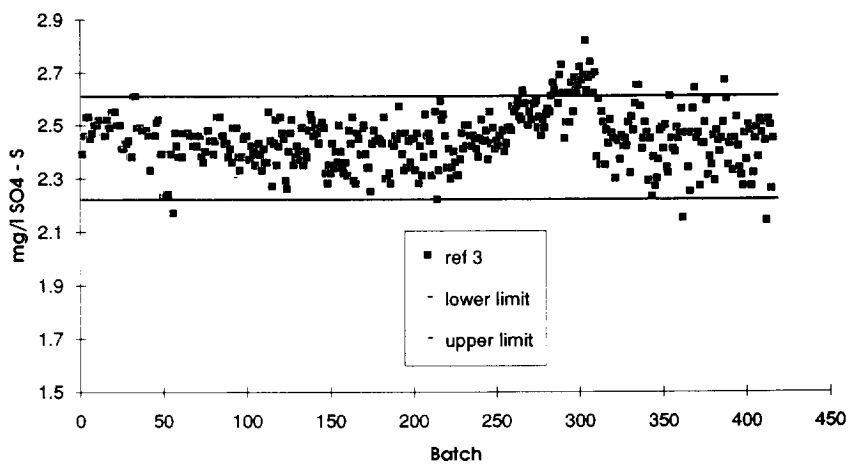

Fig. 4. Shewhart plot of SO_4^{2-} qc reference sample 3 values obtained over a period of 2.5 years.

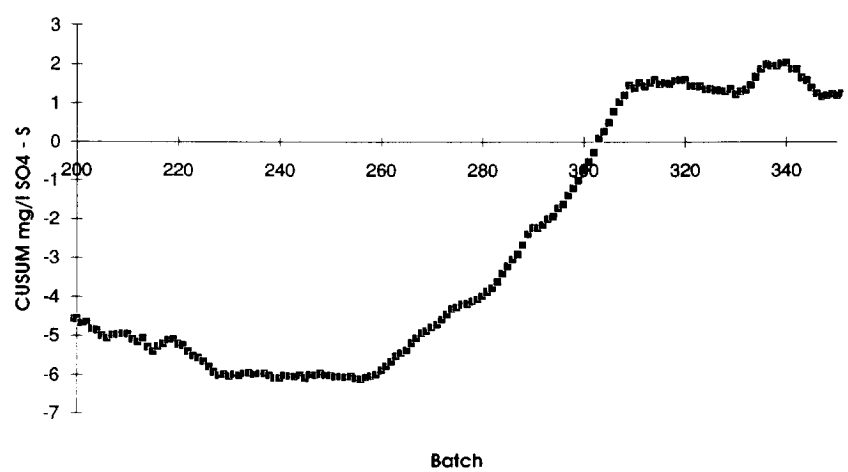

Fig. 5. CUSUM plot of SO_4^{2-} qc reference sample 3 values.

value, it is noticeably much easier to visualise the occurrence of a problem in the method with CUSUM charts, enabling the operator to detect the bias at a much earlier time than with Shewhart charts.

It proved to be particularly difficult to trace the source of the bias detected by the quality control system, especially as the bias seemed to be in all three anion components but with a much greater effect on sulphate results. Initially the chromatographer checked the most obvious causes of bias such as the stock solutions, the quality control samples, calibration equipment and injection modules. Eventually the source of the bias was traced to a faulty guard column.

Measures of accuracy

As part of the whole quality system, accrediting agencies insist on participation in proficiency testing schemes in order to assess proficiency against the wider analytical community. In the UK, the Water Research Centre (WRc) operate the AQUACHECK scheme to which nearly 400 laboratories from the water supply industry and research institutes subscribe.

Participation in a recognised proficiency testing scheme provides an external measure to link to internal quality control procedures, adds confidence to internal quality control procedures and provides a single point measure for detecting gross differences from the wider analytical community. It is important that samples received as part of a proficiency testing exercise are analysed using normal routine procedures in order that the data obtained provides an accurate picture of analytical bias.

z Scores represent an alternative way of displaying the relationship between the laboratory error and the maximum acceptable error for each determinand [z score = (result − reference value)/error threshold − z values > 1 indicate unacceptable results for monitoring drinking water]. Recent data collated from the ion chromatography tests (Table 5) show that the AQUACHECK z scores are very low for all three determinands and well below limits outlined in specifications. The bias values reported when the z score is low are not correlated with the data from the internal qc measure as all the data is within the experimental error of the method. Proficiency tests appear to provide a clear indication of significant bias from one single analysis when z scores approach unity. For smaller deviations it is possible to detect analytical differences from other laboratories over a longer period.

At a more detailed level: for Cl^-, the internal control samples indicates a different picture to the proficiency test results; NO_3^- —agree very closely with proficiency test results; SO_4^{2-} —one batch reported as 9% from proficiency test (z score very low), —in contrast within laboratory measure detected only 1% bias.

Participation in proficiency testing schemes is an important component of the overall quality system. It provides additional supporting information to validate instrumentation, methodology and internal quality control procedures. However results from inter-laboratory comparison tests should never be interpreted in isolation.

4. Conclusions

The most important aspects for controlling analytical error in anion chromatography are through establishing clear working protocols for the operation and calibration of the instrument, and through the application of robust quality control systems to validate analytical determinations.

Chemically suppressed ion chromatography of chloride, nitrate and sulphate produces non-linear calibration responses in the analytical ranges used in the analysis of environmental samples. It is recommended that multi-point calibration and a 2nd or 3rd order mathematical regression be applied to minimise calibration bias.

The integrity of the chromatography system may be maintained through routine use of sample clean-up to remove dissolved organic fractions before injection and through monitoring the guard column k' and back-pressure status. Experience has shown that interference from species which co-elute with Cl^-, NO_3^- and SO_4^{2-}

from aqueous solutions collected in ecological research are very uncommon and in low concentrations. Cross-ion interference is encountered in the analysis of extracts from soil or plant material for salt or mineral acid extractants.

A quality control system has been proposed to monitor for gross error or small shifts in bias: using two or more synthetic solutions of differing concentration; calculating mean, warning and action limits based on inter-quartile range values and reviewing the system periodically; constructing both Shewhart and CUSUM charts; rejecting data based on specified criteria (e.g. [3]) and on the basis of 2 or more qc sample values; participation in regular, well-organised inter laboratory proficiency testing schemes to validate internal qc procedures.

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