

Peak-shape analysis and noise evaluation in suppressed ion chromatography for ultra-trace ion analysis

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ABSTRACT

Numerical analysis was used to study the performance of a suppressed ion chromatographic system with on-line preconcentration for ultra-trace ion determination in ultra-pure power plant waters. Peak-shape analysis by the Edgeworth–Cramér series fitting method was applied in order to check non-linear concentration-dependent effects, so as to evaluate the best experimental practice with regard to the linear calibration range. Noise evaluation by Edgeworth–Cramér fitting residuals and Fourier analysis is discussed in order to establish the detection limits. Results of the checks made for strictly linear conditions and determination of the quantification limits for sodium, chloride and sulphate ions are reported.

INTRODUCTION

Ion chromatography (IC) is among the most recent and rapidly growing chromatographic techniques employed in inorganic and organic ion analysis [1,3]. Coupled with a preconcentration step, IC is a powerful technique for trace and ultra-trace analysis [4–8]. Among the various applications presented to date, the determination of common trace anions, such as Cl^- , SO_4^{2-} and NO_3^- , by IC seems the most promising for its sensitivity, versatility, precision and rapidity. A knowledge of parameters such as the detection limit, linearity and accuracy is of practical importance.

In ultra-trace analysis, these fundamental requirements cannot easily be satisfied from IC data or from experiments reported in the literature. In fact, the procedures and experimental conditions followed differ widely. First, the data obtained by one detection method do not correspond to those obtained by another (*e.g.*, UV data

cannot be transferred to conductivity values measured by chemical suppression). Further, noise contributions are strictly linked to the type of apparatus used (pumping system, electronics). Second, detection limits expressed as the absolute amount detected, obtained with direct injection, cannot be simply transferred to ultra-trace analysis by means of a preconcentration step. The same may also be said about linearity and all the above are also dependent on column type. A third point is the type of signal measured, peak height or peak area, and the way in which these signals are detected (*e.g.*, manual measurement, integration device or other more complex computational methods). Moreover, attention must be paid to the way in which the detection limits are obtained (*e.g.*, extrapolation method, simple noise structure evaluation) [9].

Although there is general agreement in accepting a large linear dynamic range for the IC technique [10–13], a wide linearity range in ultra-trace analysis is not often required. What is more important is a reliable calibration, which proves difficult to achieve in the ppt and ppb^a ranges because of uncontrolled contamination, wall memory and matrix effects. The best results are obtained by using a completely automatic system including both the sampling and calibration steps, thus preventing sample contamination from the environment. Such a system for on-line ultra-trace ion monitoring in the power plant “condensate–feedwater” cycle has already been described by Balconi *et al.* [14]. By processing linear calibration plots, they obtained linearity ranges and detection limits. The data reported proved to be dependent on the calibration range. For example, for SO_4^{2-} the detection limit is as low as 0.3 ppb in the concentration range 0–10 ppb, but it becomes 6.7 ppb if the concentration range is more extended (to 200 ppm).

These data are contradictory, but this is only apparently so. They reflect the overall determination error, which includes many error sources (*e.g.*, sample handling, sensitivity drift of the instrument and even the non-linearity of some parts of the analytical procedure such as the preconcentration or stripping step). All these factors remain hidden in the overall estimated procedure error unless a careful experimental design is planned in order to isolate the different error sources. Obviously such an analysis is very time consuming and costly, not only because of the large number of factors that must be kept under control, but also because detecting non-linearity effects over a linearity trend requires close, continuous control of the independent variables.

In this paper, a different approach to linearity and detection limit determination is reported for the same ultra-trace ion monitoring system mentioned above. It consists in controlling all the information contained within the analytical signal (chromatographic peak) rather than an individual part of it, such as just considering the peak area or peak height. In practice, a complete peak-shape analysis using the Edgeworth–Cramér (E.C.) series fitting method [15–17] is applied in order to compare peak shapes for different injected amounts and to detect the onset of concentration-dependent, non-linearity effects [18]. In this manner, complementary, but conceptually different, information is obtained which can more clearly aid in understanding the previously reported experimental results [14] and can also give indications as to how to improve the method.

^a Throughout this article, the American trillion (10^{12}) and billion (10^9) are meant.

As the chromatographic signal is always affected by unwanted noise components of a random or deterministic nature which reduce the instrumental detectability, characterization of the noise by Fourier analysis was the second point studied. In fact, a knowledge of the noise structure not only makes it possible to define unambiguously method detection limits but also suggests how to improve them by filtering or instrumental improvements [19].

The results obtained in this study obviously cannot be extended to entirely different experimental conditions; however, to date, very few linearity studies have been reported using rigorous peak-shape analysis and, of these, none simultaneously report a study of the noise. The advantages and the drawbacks of such an approach will also be interesting for different chromatographic fields.

EXPERIMENTAL AND DATA HANDLING

Chromatographic analyses were performed with a Dionex (Sunnyvale, CA, USA) Qic ion chromatograph. Experimental conditions for cation and anion determinations are given in Table I. Dionex concentration columns (50×3 mm I.D.), TCC-1 for cations and TAC1 for anions, were connected to the injector instead of the sample loop for sampling with preconcentration. Enrichment factors of 250 for anions and 125 for cations were applied. Analytical-reagent grade chemicals (Merck, Darmstadt, Germany; Baker, Philipsburg, NJ, USA) were used and standard solutions were prepared by on-line dilution with power plant water of the best quality and also with the water obtained from a Millipore (Milford, MA, USA) Milli-Q water purification system (background ion concentrations in power plant water: Cl^- ca. 5 ppb, Na^+ and $\text{SO}_4^{2-} \leq 5$ ppb). Standard solutions of sodium, chloride and sulphate ranged from 10 to 200 ppb.

The detector signal was digitized at a rate of 4 data per second using an HP 3455A model voltmeter (Hewlett-Packard, Avondale, PA, USA). The data were transferred to a mainframe computer for E.C. series fitting by means of a non-linear least-squares minimization procedure. Noise was evaluated by a boxcar five-point

TABLE I

EXPERIMENTAL CONDITIONS FOR ION CHROMATOGRAPHIC ANALYSIS

Samples: sodium, chloride and sulphate. Concentration range: 10–200 ppb.

Parameter	Anion determination	Cation determination
Preconcentration column	HPIC-AG4	CGI
Separation column	HPIC-AS4	CSI
Suppression column	AFS ^a	CFS ^a
Eluent	2 mM NaOH–3 mM Na ₂ CO ₃	5 mM HCl
Regenerant	0.0125 M H ₂ SO ₄	0.04 M TMAOH ^b
Eluent flow-rate (ml min ⁻¹)	2	2.3
Regenerant flow-rate (ml min ⁻¹)	2.5–3	2.5–3
Sampling time (min)	10	5
Sampling rate (ml min ⁻¹)	2.5	2.5
Conductimeter range (μS)	100	100

^a Dionex fibre suppressor.

^b Tetramethylammonium hydroxide.

cubic least-squares approximation on digitized data according to a Fortran IBM (IBM Instruments, Danbury, CT, USA) routine [20] and by computing the root-mean-square deviation between experimental (YE) and smoothed (YS) data:

$$N_{\text{RMS}} = \sum_{i=1}^{N_p} (YE - YS)_i^2 / (N_p - 1)^{1/2} \quad (1)$$

where N_p is the number of data points.

For analysed peaks (standard deviation range 10–40 s) the smoothing window proved to be 1.2 s. The signal-to-noise ratio (S/N) was measured as the ratio between maximum peak height (after removing drift and baseline contribution to signal), $YMAX$, and peak-to-peak noise, computed as four times the N_{RMS} value [9]:

$$S/N = YMAX/4N_{\text{RMS}} \quad (2)$$

As N_{RMS} is taken as the standard deviation of the “analytical blank”, the quantification limit (L_q), defined as the concentration that provides a signal 20 times the blank [21], is computed from eqn. 2 as

$$L_q = \frac{5c}{S/N} \quad (3)$$

where c is the concentration of the analyte solute. Peak parameters were obtained as explained previously [15]. All calculations for peak-shape analysis were run on a CDC Cyber 76 computer (Cineca, Casalecchio, Bologna, Italy). Fourier analysis was performed on an M24 personal computer (Olivetti-Italy) applying the fast Fourier transform (FFT) procedure according to the Cooley–Tukey algorithm [22], to digitized peak data by using the Labtech Notebook software (Laboratory Technologies, Wilmington, MA, USA). Noise was reduced by filtering in the Fourier domain using a rectangular low-pass filter as discussed under Results and Discussion.

THEORY AND PROCEDURE

An experimental chromatographic peak, considered as a time function signal $y(t)$, can be related to a frequency function $f(x)$, normalized to unit area and unit width, as follows:

$$y(t) = f(x) A/\sigma \quad (4)$$

where σ is the peak standard deviation and area A and the normalized time variable x are defined as follows:

$$A = \int_{-\infty}^{+\infty} y(t) dt \quad (5)$$

$$x = (t - m)/\sigma \quad (6)$$

where m is the peak mean.

The E.C. series asymptotic expansions, developed to the K th order [23], make it possible to approximate a chromatographic peak expressed as a frequency function $f(x)$ for linear non-ideal chromatography according to the following equation:

$$f(x) = Z(x) + \sum_{v=1}^K Q_v(-Z) + R_K(x) \quad (7)$$

where $Q_v(-Z)$ is a linear aggregate of the derivatives of the normal frequency function $Z(x)$, maximum order $3v$, and contains the cumulant coefficients, of maximum order v , of the frequency function $f(x)$ [23]. Of particular interest in peak-shape characterization are the first two cumulant coefficients, namely the skewness (S) and the excess (E). They measure the peak asymmetry and the degree of peak flattening, respectively. For normal curves, the S and E values are both zero. For tailed peaks, skewness values are positive and conversely for fronted peaks; excess values are positive when the peak is more tall and slim than the normal curve and conversely in the opposite case. Detailed expressions for $Q_v(-Z)$ terms and cumulant coefficients are reported elsewhere [15,23].

The remainder, $R_K(x)$, is a function showing a structured behaviour: *e.g.*, the number of nodes increases as the K -grade rises, and this is almost symmetrical with respect to $x = 0$. The residual function is practically expressed as a percentage difference, $D\%$, between experimental (YE) and calculated E.C. series expansion (YC) peak data. This is defined *versus* the normalized time variable, x , as follows:

$$[D\%(x)]_K = [YE(x) - YC_K(x)] \cdot 100/YMAX \quad (8)$$

Using a non-linear least-squares fitting procedure, an unbiased estimate of statistical peak parameters (area A , mean m , variance σ^2 , skewness S , excess E and other cumulant coefficients: γ_3 , γ_4 , etc.) is made with satisfactory precision [15,16]. Fitting can be evaluated by the mean approximation error, $CV\%$, which is the coefficient of variation of the fitting at the peak maximum in percent [15]:

$$(CV\%)_K = \left[\sum_{i=1}^{N_p} (YE - YC_K)_i^2 / (N_p - n_p - 1) \right]^{1/2} \cdot (100/YMAX) \quad (9)$$

where N_p and n_p are the number of points and the number of parameters, respectively. The approximation degree of a peak can also be estimated by the approximation-to-noise ratio (ANR) parameter, defined as

$$ANR_K = \left[\sum_{i=1}^{N_p} (YE - YC_K)_i^2 / (N_p - n_p - 1) \right]^{1/2} / N_{RMS} \quad (10)$$

where N_{RMS} is the root-mean-square noise defined by eqn. 1. As residuals include the non-fitting of the E.C. series and the system noise [15,23], $ANR = 1$ only when fitting residuals are exactly consistent with noise. High ANR values suggest that incomplete fitting makes a contribution within residuals.

On increasing the series expansion order, the peak approximation improves (lower $CV\%$ values) up to a maximum level, depending on the peak shape (skewness) and the signal-to-noise ratio [17]. It has been proved that, under linear chromatographic conditions, E.C. series fitting is able to approximate peaks in a skewness range from 0.03 up to 0.8 with $CV\%$ values ranging between 0.002% and 1% [17].

In the E.C. series fitting pattern, four rules are to be considered when evaluating the goodness of a fit:

(1) for peaks with skewness values < 0.8 , there must be consistency between maximum expansion order (K_{\max}), noise values and skewness values; K_{\max} increases with increasing S and noise [17];

(2) under best-fit conditions, the residual values must be consistent with the intrinsic noise level, as reported previously [17]; the residual analysis provides information about the IC system noise;

(3) the statistical parameters (A , m , σ^2 , S , E , γ_3 , γ_4 , ...) calculated by fitting are almost stable when K is increased to its optimum value and, further, they do not depend on solute concentration [18];

(4) for very skewed peaks ($S > 0.8$), an increase in expansion order K , even over 3–4, does not decrease the $CV\%$ value, nor does it improve fitting; under these conditions the peak parameter values obtained from the fitting are meaningless [17].

The simultaneous consistency of the general features mentioned above is a necessary condition for a linear non-ideal chromatographic process. A breakdown of these conditions when the amount injected is increased usually signifies the onset of non-linearity effects. Such behaviour has been demonstrated for both theoretically generated peaks [17] and different experimental systems such as gas chromatographic packed and capillary columns [18,24] and also field flow fractionation peaks [25]. Graphic peak-shape analysis is also useful in checking non-linearity effects [24,26]. In fact, the peak shape, and statistical peak parameters, must remain the same as concentration is increased until the chromatographic process reaches non-linear conditions.

Fourier analysis is a well known procedure for analysing the frequency components of waveforms, not necessarily periodic, such as chromatographic peaks. By converting the time domain (t) signal to its frequency (ν) counterpart, a chromatographic signal has its own unique frequency spectrum where peak information is usually at lower frequencies than the noise components [19]. In the frequency domain noise frequencies can thus be removed by using a digital low-pass filter [27,28].

Various methods have been considered for determining the appropriate cut-off frequency. The first, suggested by Maldacker *et al.* [29], takes as the cut-off frequency the point at which the Fourier power spectrum amplitude, $F^2(\nu)$ [27], drops to less than 0.1% of the maximum. The second method involves the concept of the equivalent width time (EWT) [22]. This quantity is calculated from area A and height $YMAX$ of the peak to be filtered as follows:

$$EWT = A/YMAX \quad (11)$$

The cut-off frequency is the reciprocal of the EWT parameter as described by Lam and Isenhour [30]. The last method, applied by Bush [31], takes as the cut-off frequency the point at which the standard deviation of the Fourier power spectrum amplitudes, computed from higher to lower noise components, remains constant.

The filtering performance of these methods was evaluated by computing the root-mean-square (RMS_F) difference between experimental (YE) and filtered (YF) signals as follows:

$$RMS_F = \left[\sum_{i=1}^{N_p} (YE - YF)_i^2 / (N_p - 1) \right]^{1/2} \quad (12)$$

RESULTS AND DISCUSSION

Linear range determination by peak-shape analysis

Ion chromatographic peaks, here collected and analysed under different experimental conditions, are the outputs of a complex ion trace analysis apparatus which includes the following steps: preconcentration, stripping and injection, separation and detection. For a critical evaluation of the overall linearity of this analytical procedure, the E.C. series fitting method provides two key tools: peak parameters and peak shapes.

Table II reports the numerical results of peak-shape analysis for sodium, chloride and sulphate ions under different concentrations. The statistical peak parameters, signal-to-noise ratio (S/N), coefficient of variation of the fitting ($CV\%$) and approximation-to-noise ratio (ANR) are listed for the series expansion order of the best fitting (K_{max}).

The S/N values at which different peaks were recorded increased with increase in concentration, as expected since noise is approximately constant whereas the signal increases as the amount analysed is increased. In contrast the approximation degree of the E.C. series fitting ($CV\%$) does not improve at the same rate. In particular for Cl^- and SO_4^{2-} , it worsens as the concentration increases. ANR expresses more clearly the progressive inability of the E.C. series to approximate Cl^- and SO_4^{2-} peaks at

TABLE II
PEAK PARAMETERS BY THE E.C. SERIES FITTING METHOD

Parameters: c = analysed concentration; σ^2 = variance; S = skewness; E = excess; K_{max} = optimum E.C. series expansion order; S/N = signal-to-noise ratio; $CV\%$ = fitting coefficient of variation (%); ANR = approximation-to-noise ratio.

Ion	c (ppb)	σ^2 (s ²)	S	E	K_{max}	S/N	$CV\%$	ANR
Na ⁺	11.5	301	0.31	0.78	6	108	0.58	2.5
	113.5	317	0.19	0.63	4	1050	0.22	9.3
	225.5	323	0.24	0.74	6	1350	0.28	15
Cl ⁻	10.2	121	0.46	0.55	4	374	0.19	2.8
	10.2	126	0.52	0.85	6	318	0.34	4.3
	100.5	136	0.73	1.61	5	2190	0.72	63
	200.0	127	0.78	1.75	5	4180	0.93	156
SO ₄ ²⁻	10.2	1480	0.26	0.31	6	68	0.49	1.3
	100.5	1508	0.68	0.82	6	480	0.28	5.4
	200.0	1644	0.71	1.73	5	1495	0.72	43

increasing concentrations. In fact, this quantity is very low for Cl^- only at 10.2 ppb and for SO_4^{2-} only at 10.2 and 100.5 ppb (see Table II).

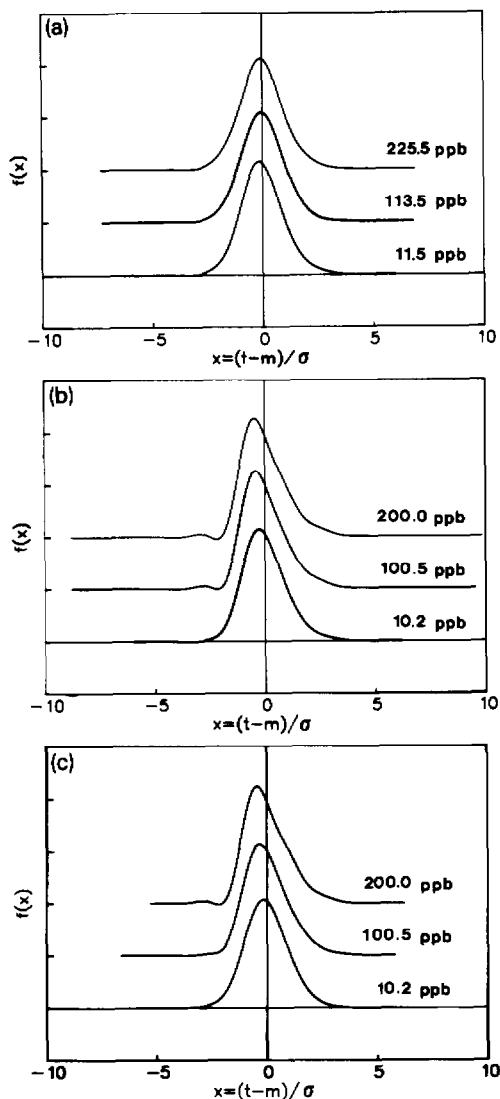
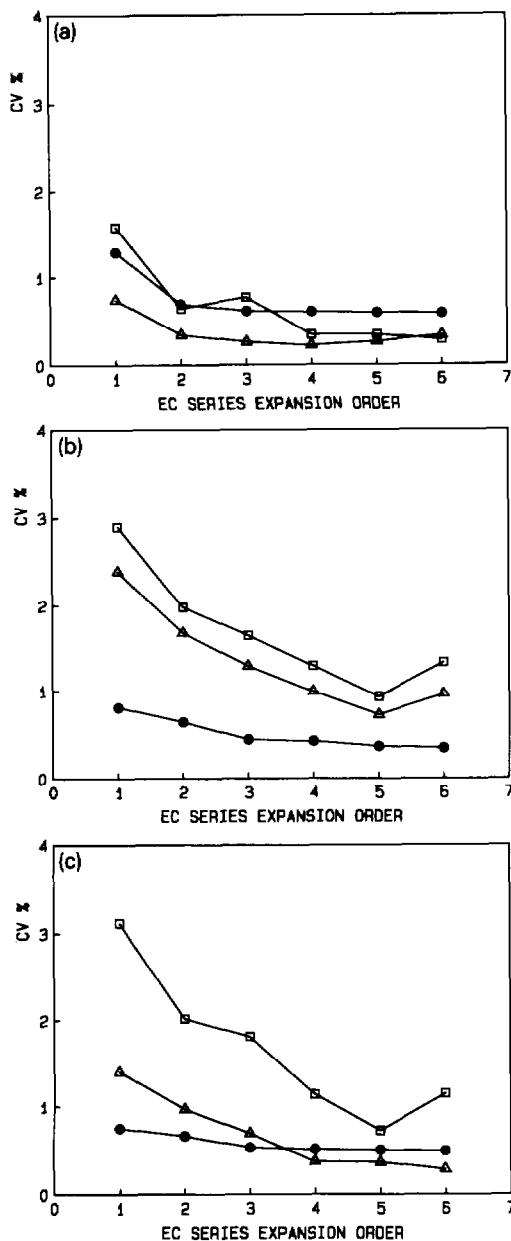


Fig. 1. Fitting coefficient of variation ($CV\%$) vs. E.C. series expansion order at different concentrations: (a) sodium (● = 11.5 ppb; △ = 113.5 ppb; □ = 225.5 ppb); (b) chloride (● = 10.2 ppb; △ = 100.5 ppb; □ = 200.0 ppb); (c) sulphate (● = 10.2 ppb; △ = 100.5 ppb; □ = 200.0 ppb).

Fig. 2. Normalized fitted peaks vs. the normalized time variable (x) at different concentrations: (a) sodium; (b) chloride; (c) sulphate.

Let us now analyse in detail the E.C. fitting patterns as the series expansion order increases. In Fig. 1, the $CV\%$ for the ions considered at different concentrations is plotted against expansion order K . It can be observed that the best fitting conditions are soon obtained for all the Na^+ concentration values, even with E.C. series expansion order $K \approx 2$. A further expansion of the series only slightly improves the degree of approximation. In contrast, Cl^- behaves as Na^+ at the lowest concentration, whereas at higher values (100.5 and 200 ppb), the fitting minimum is found only when the expansion order has reached a value of 5. Sulphate behaves like chloride

The skewness and excess parameters behave similarly to $CV\%$: with Na^+ these parameters are independent of both concentration and E.C. series expansion order, whereas for Cl^- and SO_4^{2-} this does not hold true except at concentrations lower than 10.2 ppb.

In order to establish exactly to what extent the fitting pattern is or is not congruent with the intrinsic properties of the E.C. series, and thus to check non-linear behaviour, reference can be made to the simulation study cases analysed elsewhere [17]. Peaks generated by theoretical peak-shape functions in linear chromatography and having skewness values comparable to those encountered here, should be approximated with a $CV\%$ value lower than 0.3%. This behaviour is obeyed by Na^+ at all the concentrations considered, whereas Cl^- and SO_4^{2-} have this property only at the lowest concentration analysed (10.2 ppb). E.C. series, applied to fit Cl^- and SO_4^{2-} peaks at higher concentrations, behave as a fitting function without precise meaning.

Graphic peak-shape analysis pictorially represents the previously described evidence. In Fig. 2 a comparison of fitted peaks, normalized at unit area, at different concentrations is shown for the ions considered. Whereas the sodium peak shape remains the same, the peaks of both anions do not maintain the same shape with respect to concentration.

The inability of the E.C. series to approximate non-linear cases is even clearly seen in the oscillatory nature of the fitting residual function, $D\%$, shown in Fig. 3. Note also that in the cases which were recognized as "linear", the degree of fitting is not only good but also homogeneous over the whole peak and with a large number of nodes, as expected from the properties of E.C. series [15]. This does not hold true in those cases of non-linearity.

It can be observed at this point that it is the oscillatory behaviour of the E.C. series which prevents the residual from being identical with the noise, even under the best approximation conditions (see the Na^+ case). Thus the ANR values reached (ranging between 2 and 15; see Table II: Na^+ cases, Cl^- at 10.2 ppb, SO_4^{2-} at 10.2 and 100 ppb) are to be considered as much more than acceptable.

From the results presented, it can be concluded that E.C. series peak-shape analysis is unambiguously able to detect linearity limits. The linearity limits determined here are identified as the highest concentration where the E.C. series is able to approximate the response peak shape coherently. Such values, 200 ppb for sodium and 10 ppb for chloride and sulphate, appear much lower when compared with linearity ranges reported elsewhere for IC with or without preconcentration.

Wetzel *et al.* [4] reported linear dynamic ranges of 10^4 for phosphate, nitrate and sulphate from 2 to 10^4 ppb and of 10^3 for chloride from 2 to 10^3 ppb; Haddad and Heckenberg [3] investigated the linearity for other anions (nitrite, nitrate and bromide) between 0 and 20 ppb. These values were determined using peak height or

area, which can be linear over a broader concentration range than that determined here, whereas the peak-shape analysis is a more sensitive approach and is much more stringent with respect to concentration effects than is either peak area or peak height.

Taking into account what has been reported elsewhere about linearity in IC [3,4,10–13], the origin of the non-linearity, detected here especially for Cl^- and SO_4^{2-} , cannot be ascribed to the separation column, but to other instrumental components of the considered IC system. A detailed investigation on the single band broadening and tailing contributions due to different extra-column effects is beyond the aims of this work.

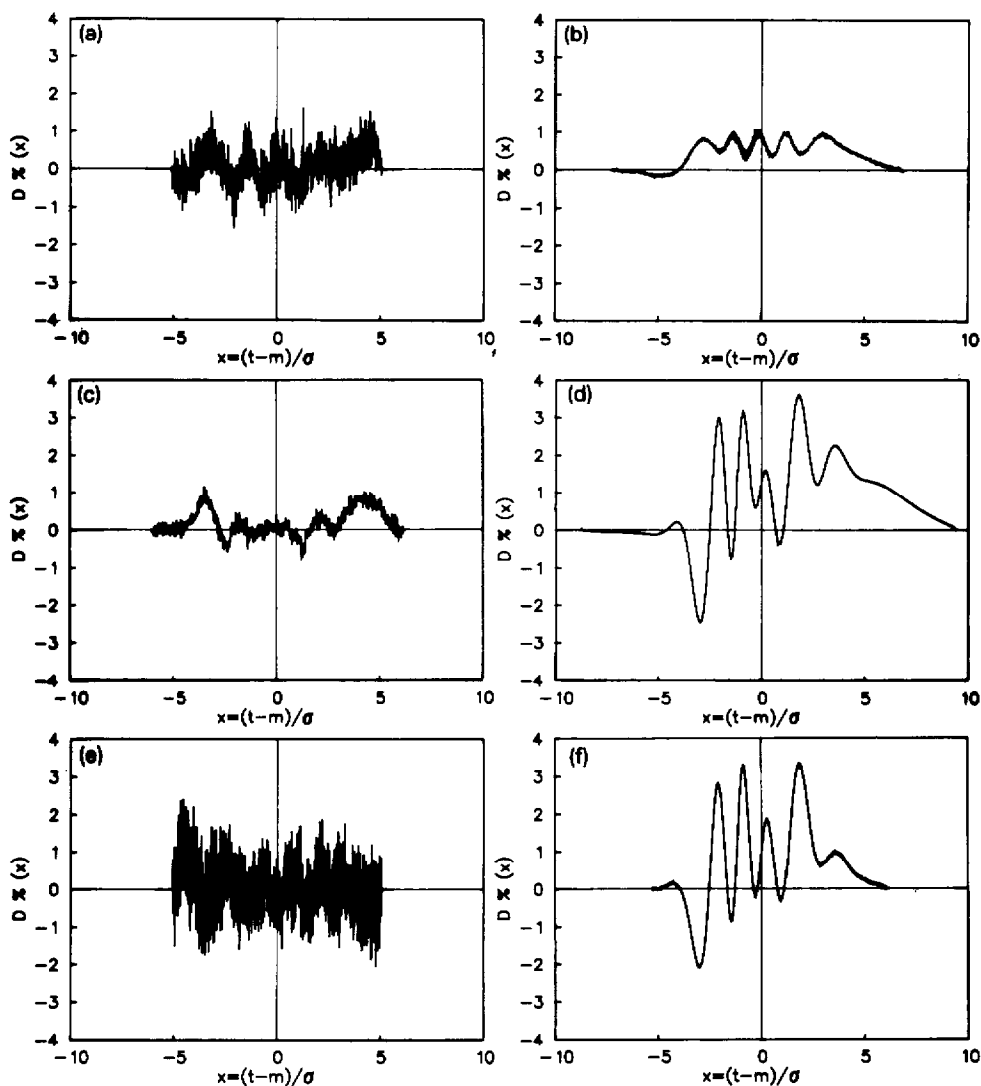


Fig. 3. Residuals of the best E.C. series fittings vs. the normalized time variable (x): (a) sodium, 11.5 ppb; (b) sodium, 225.5 ppb; (c) chloride, 10.2 ppb; (d) chloride, 200.0 ppb; (e) sulphate, 10.2 ppb; (f) sulphate, 200.0 ppb.

Noise analysis and quantification limits

As the chromatographic signal has been approximated at its best and a linear range is made evident, it can be assumed that this status also holds true at lower concentrations and that quantification limits are consequently determined by the existing noise. First information regarding system noise is included in the residual function $D\%$ by virtue of its peculiar properties. In fact, $D\%$ plots (Fig. 3) exhibit three different components: high-, intermediate- and low-frequency terms. The first

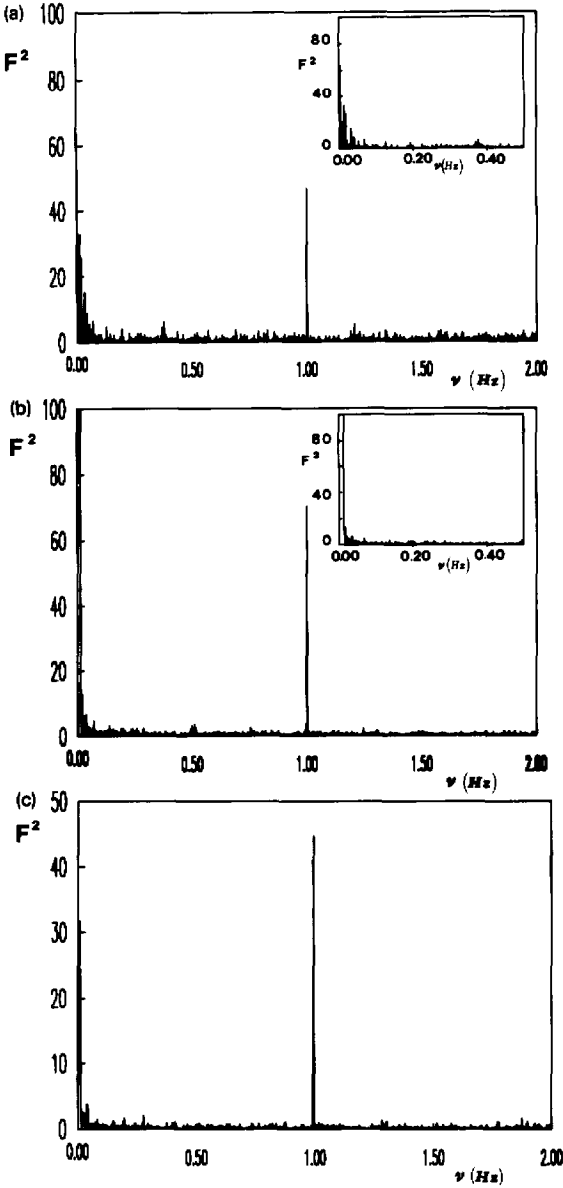


Fig. 4. Fourier power spectra of chromatographic signals: (a) baseline; (b) sulphate, 10.2 ppb; (c) its E.C. fitting $D\%$ residual.

TABLE III
 QUANTIFICATION LIMITS IN ION CHROMATOGRAPHY WITH ON-LINE PRECONCENTRATION

Enrichment factor: 250 (anions); 125 (cations).

Ion	L_q (ppb)	
	Without FFT filtering	With FFT filtering
Na ⁺	0.5	0.030
Cl ⁻	0.1	0.007
SO ₄ ²⁻	1	0.080

two components can be explained as noise contributions. The last, however, arises from the kind of fitting considered (E.C. series) and becomes more evident when the signal-to-noise ratio rises and the other two components become negligible.

In order to characterize in detail the noise structure on the chromatographic signal, the fast Fourier transform procedure (FFT) was applied to the baseline, to peaks and also to residuals of the E.C. series fitting. Each chromatographic signal is described by its power spectrum in the frequency domain.

Fig. 4 shows the power spectra of (a) the baseline, (b) an SO₄²⁻ peak at 10.2 ppb and (c) the corresponding E.C. fitting D^0 residual. The peak frequency components (peak information) are located at the lowest frequencies whereas noise components spread at higher frequencies. The last correspond in all spectra to the white type of noise. The sharp noise component present at 1 Hz is related to the eluent pumping system of the kind of chromatograph used; it is present in all power spectra and proves to represent a deterministic noise component.

The precision level having been set, the quantification limit can be obtained by defining it as the concentration that provides a certain signal multiple of the noise (see eqn. 3). Several quantification limits can be defined in this manner, depending on what is taken as the noise. In the present instance the noise component at 1 Hz, clearly deterministic, is far from the low-frequency signal components and can easily be eliminated. In order to reduce noise appropriately, the use of a low-pass filter in the

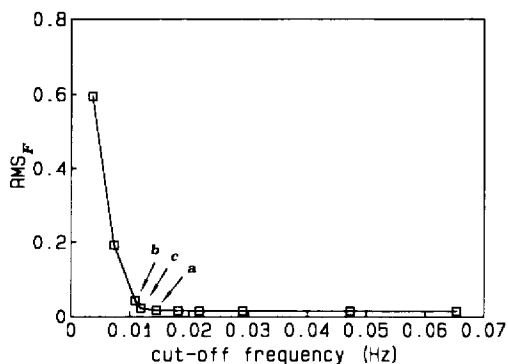


Fig. 5. Root mean square difference (RMS_F) between original and filtered signals vs. cut-off frequency: sulphate peak, 10.2 ppb; (a) 0.1% of power spectrum maximum criterion; (b) *EWT* criterion; (c) constant power spectrum amplitude standard deviation criterion.

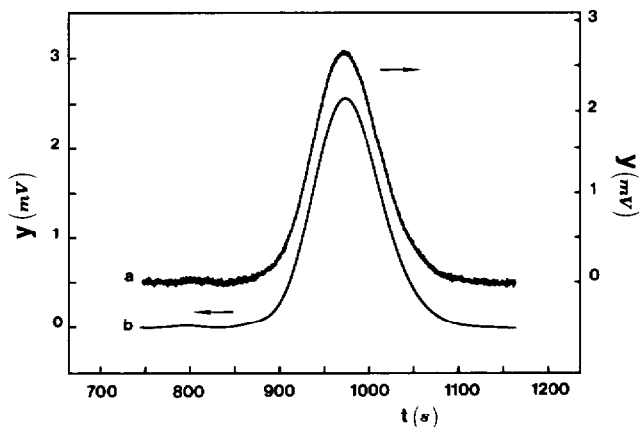


Fig. 6. Filtering: sulphate peak, 10.2 ppb; cut-off frequency 0.015 Hz: (a) original peak; (b) filtered peak.

frequency domain is considered. To select the optimum cut-off frequency, the three different criteria described under Theory and Procedure were applied [(a) power spectrum amplitude $< 0.1\%$ of the maximum; (b) reciprocal to the EWT parameter; (c) constant standard deviation of the power spectrum amplitudes].

In Fig. 5, the RMS_F difference between the original and filtered peaks vs. the cut-off frequency is plotted for an SO_4^{2-} peak at 10.2 ppb and the three criteria labelled as a, b and c are shown. It can be seen that the cut-off graphically determined according to criterion c provides the lowest RMS_F value among the three methods applied. At the same time this filtering is satisfactory as it preserves the original peak shape, as can be seen in Fig. 6 where the original and filtered sulphate peaks are shown. By this filtering procedure, the signal-to-noise ratio is obviously enhanced and it has been estimated that it can be improved at least 20-fold. Under the latter safe condition, allowance is also made for a limited signal drift. On this basis two hypotheses of quantification limits are reported in Table III. The first is computed according to eqn. 3 and the second is a value enhanced 20-fold if the filtering procedure is employed. It can be seen that the quantification limits determined by this approach appear significantly lower than those obtained by linear calibration plots [14].

CONCLUSIONS

IC with a preconcentration step appears to be a very sensitive method for ultra-trace ion determinations. The peak-shape analysis, employed here to check anomalous concentration-dependent behaviours, even minimal, in the overall analytical system, proved to be a powerful tool in determining the correct linearity range, in order to plan the routine use of the IC technique, e.g., in ultra-trace ion monitoring in power plant "condensate-feed water" cycle already described [14].

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