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Journal of Chromatography A, 833 (1999) 97–104

JOURNAL OF  
CHROMATOGRAPHY A

Short communication

## Routine check of baseline noise in ion chromatography

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Received 2 October 1998; received in revised form 12 November 1998; accepted 16 November 1998

### Abstract

The long-term check of baselines in an ion chromatograph for more than two years reveals that the suppressor breakdown and solvent contamination can be detected by the anomalous patterns of the power spectra of the baseline noise. The signal is not referred to in this study. The early detection of the troubles is possible and the quality of a new suppressor can also be examined by the noise pattern. Coupled with the signal information such as shape and elution time, the above methodology will provide a rapid and reliable routine check for ion chromatography. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Baseline noise; Noise

### 1. Introduction

The routine check of analytical instruments should provide a sufficient amount of evidence to judge the reliability of the daily results of instrumental analyses, but, at the same time, be simple and rapid. A serious problem of the routine check is that the time for check and information on the instrumental daily conditions seem to be a trade-off in a practical sense. As an example, a good criterion for validation, etc., is the limit of detection (LOD), which is usually determined from the average of area measurements (signal) and standard deviation of blank measurements (noise) [1–7]. Unfortunately, the high reliabili-

ty of the LOD estimates requires many replicates (and much time).

This paper retrospectively analyses the daily check results of an ion chromatography (IC) system over two years. In principle, the daily check based on the information on either signal or noise can overlook some malfunctions, and the information on both signal and noise is inevitable for complete checking. Nevertheless, this paper discloses that suppressor breakdown and solvent contamination can be detected from the anomalous pattern of noise power spectra without recourse to the signal information.

We can suspect some instrumental malfunctions, if the pattern of the noise power spectrum is different from the usual one. The time for acquiring the power spectrum is usually short. For example, the sampling intervals of an analog-to-digital converter in our system are 0.2 s and the acquisition time of the

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baseline of 2048 data points is no more than 7 min. This simple, rapid method cannot cover most of the troubles, but provides a new direction for the routine check.

## 2. Experimental

All chemicals were purchased from Wako.

A Dionex DX-300 ion chromatograph was equipped with an AGP pump, CDM-3 conductivity detector and 100- $\mu$ l loop injector. A Dionex IonPac CS14 analytical column (250 $\times$ 4 mm) was used with an IonPac CG14 guard column (50 $\times$ 4 mm). The mobile phase was 10 mM methane sulfonic acid and the flow-rate was 1.0 ml/min. A CSRS-I cation

self-regenerating suppressor was used in the recycle mode. The sampling interval of the analog-to-digital converter was 0.2 s.

The power spectra of the baselines were obtained by a laboratory-made computer program called TOCO (Total Optimization of Chemical Operations). The baselines of 2048 data points each are used for the noise power spectra.

## 3. Theory

In order to express the anomaly of the power spectrum in a numerical way, we rely on a  $1/f$  fluctuation model called the FUMI theory (Function of Mutual Information) [8,9]. In this model, the  $1/f$

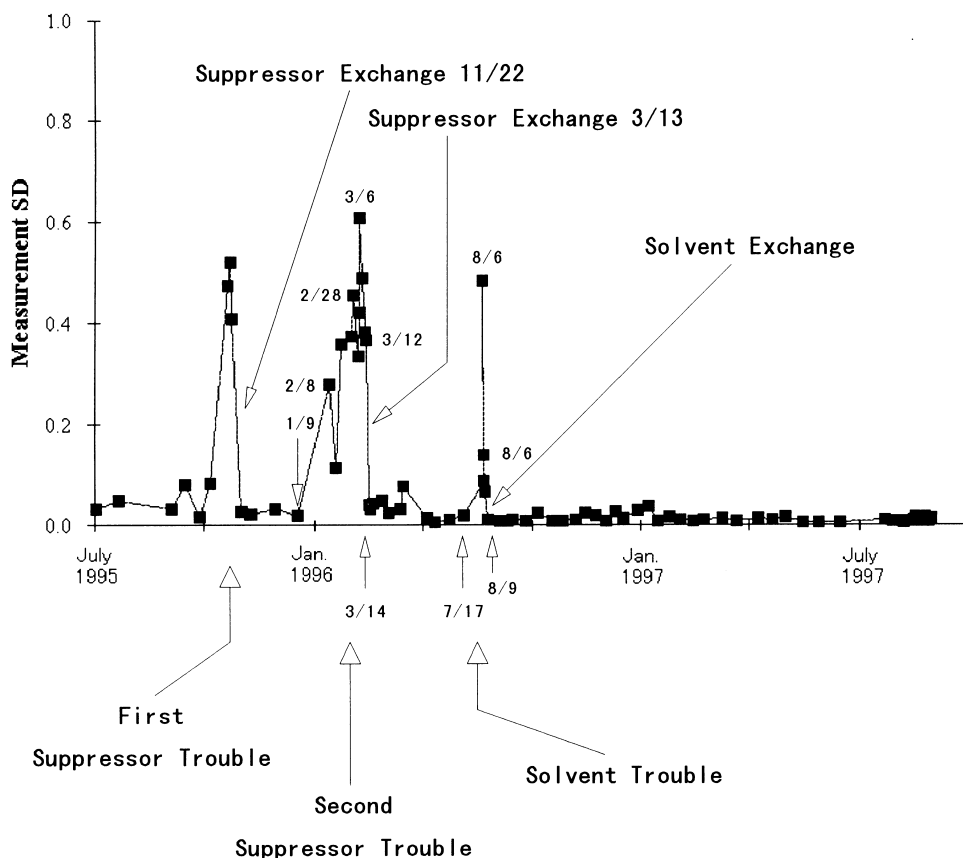


Fig. 1. Long-term routine check of the ion chromatograph. The dates on which the baselines were observed are shown in Figs. 1–6. The integration domain consists of 49 data points and the zero window of 10 data points (no lag time). The zero line for the integration is drawn horizontally.

fluctuation is approximated by the white noise and Markov process which are typical random processes in spectral analysis. The least-squares fitting of the model random processes to the actual power spectrum of the baseline produces a parameter concerning the measurement uncertainty. This uncertainty means the standard deviation (S.D.) of area measurements and is used as a criterion of the routine check throughout this paper.

The baseline (noise) looks different each time it is observed, even if the ambient and instrumental conditions are controlled as perfectly as possible. Many studies, however, demonstrate that the noise power spectra of most instruments have the general pattern called  $1/f$  noise ( $f$  means frequency) [1,10–12] and that the noise power spectrum of every instrument has a  $1/f$ -like pattern of its own. That is,

the power spectrum of a single baseline provides knowledge concerning all the baselines in the instrument (called population in statistics). The knowledge that the FUMI theory extracts from the single power spectrum is the measurement S.D. which represents the property of the population. Therefore, the repeated measurements are unnecessary for obtaining the statistical quantity in the FUMI theory.

The noise amplitude (peak-to-peak or rms noise) is also available for the same purpose. It is exceptionally fast, but cannot be related to the probability that the baseline noise is mistaken for the signal, unless the noise is the simplest (white noise). This probability is the fundamental concept of the LOD [4,5,9]. This paper adopts the FUMI theory which can directly derive the probability from the noise power spectra [8,12].

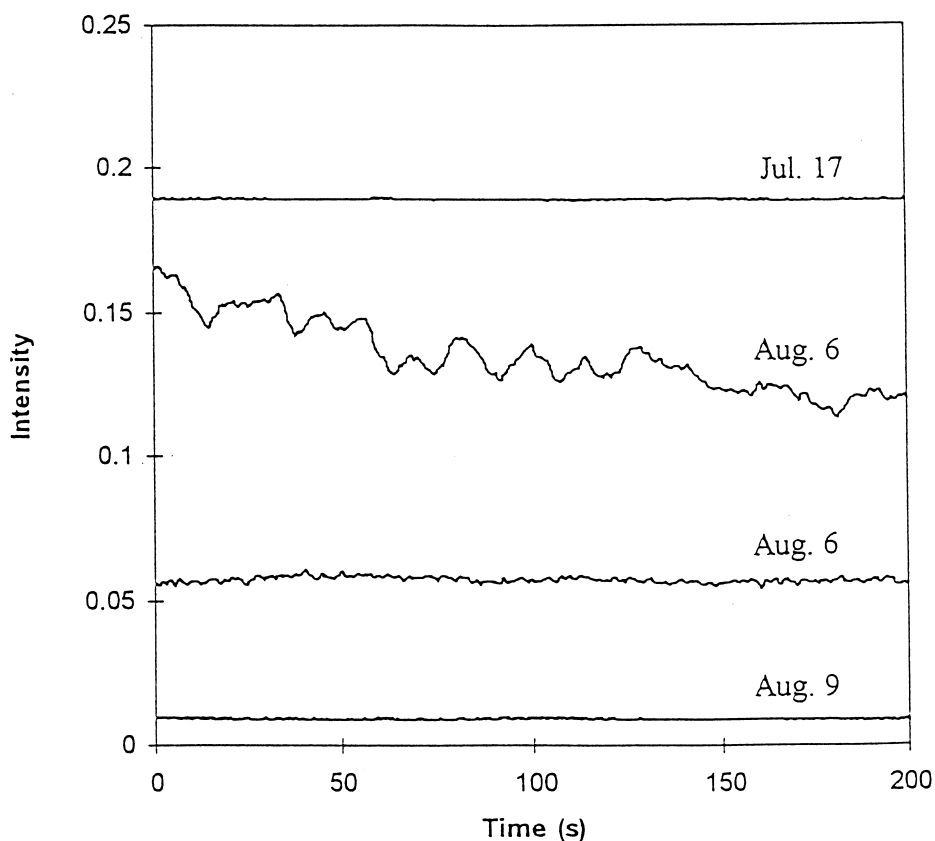


Fig. 2. Baselines for mobile-phase trouble in 1996. The dates on which the baselines were observed are shown in the figure.

#### 4. Results and discussion

Fig. 1 shows the control chart of the IC system over two years. The ordinate, measurement S.D., means the standard deviation of area measurements for a standard material. If the integration domain for the standard is predetermined according to the peak width, the FUMI theory provides the criterion (measurement S.D.) from the baseline noise. Here, the measurement S.D. depends only on the stochastic properties of the baselines, since all the parameters

concerning the signal shape (here, the integration domain, etc.) are fixed.

The control chart bears the signs of instrumental troubles in three periods (indicated by the upward arrows). At the last stage of each trouble, the results of quantitative analysis in the system were obviously erroneous. The suppressor breakdown and solvent contamination were identified by the careful inspection of the instrument. The criterion itself cannot suggest the cause of the troubles, but signals the possibility of some troubles.

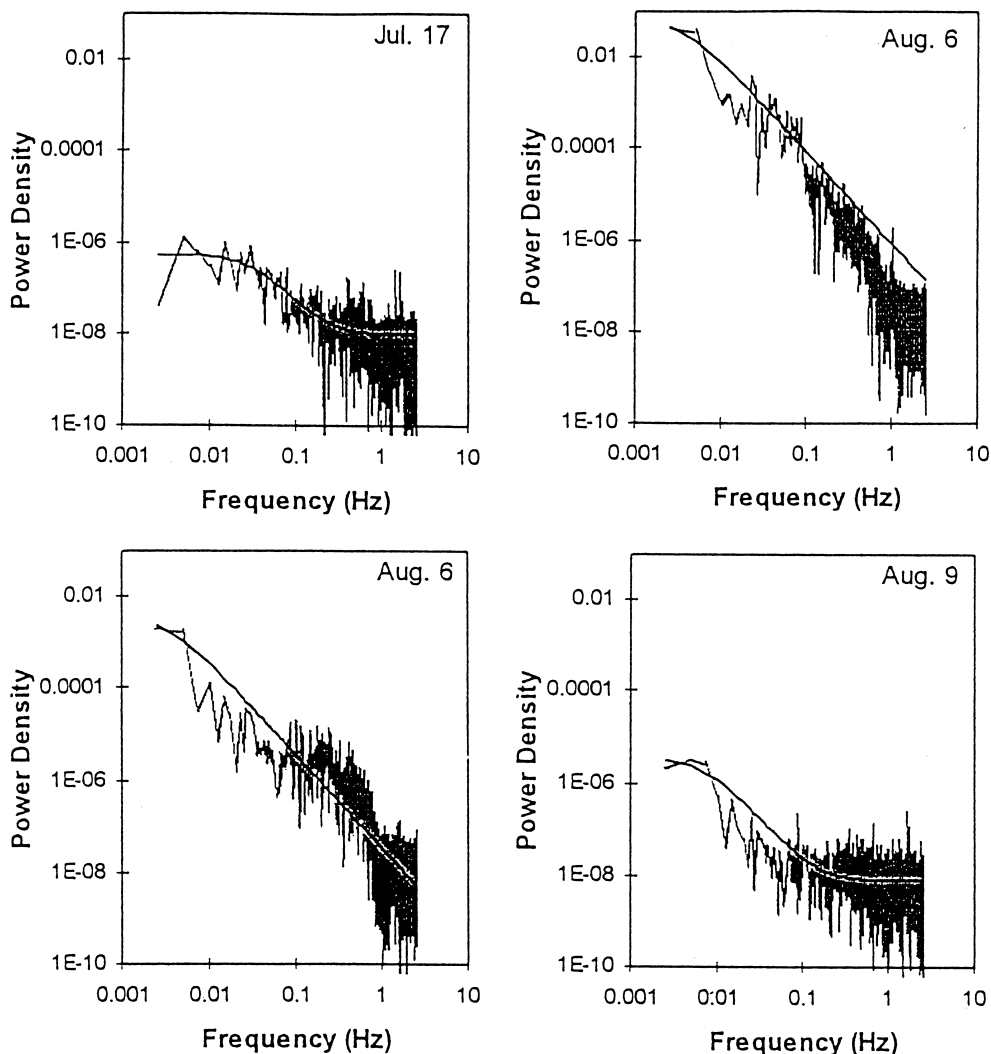


Fig. 3. Power spectra for mobile-phase trouble in 1996. The logarithm of the power density is plotted against the logarithm of the frequency. Measurement S.D.: 0.018 for 7/17; 0.48 for 8/6 (upper right); 0.14 for 8/6 (lower left); 0.011 for 8/9. The power spectra are obtained from the baselines of Fig. 2.

First, the mobile-phase trouble is explained for convenience. The baselines observed for the period of the solvent trouble are shown in Fig. 2 and their power spectra in Fig. 3 (zigzag lines). The smooth lines in Fig. 3 are the least-squares fittings of the  $1/f$  model from which the measurement S.D. is calculated.

In case of no instrumental troubles, the noise power spectra always resemble the ubiquitous  $1/f$  pattern in the long-term routine check. The baselines and power spectra of 7/17 and 8/9 are normal ( $1/f$ ). In theory, the  $1/f$  noise has a slope of  $-1$  in the log–log scale. In the IC system, however, the power spectra are always horizontal in the high frequency region ( $>0.5$  Hz) and deviate slightly from the idealistic  $1/f$  pattern. This observation is common to many instruments that are working well [8,12,13].

The extra noise components are spotted in the baselines of 8/6 (see Fig. 2). They shift the power spectra upward (see Fig. 3), resulting in the high values of the criterion. The value of the measurement S.D. (criterion) in case of the trouble (ca. 0.5) is about 10-times as large as the normal values (ca. 0.03) (see Fig. 1). The cause of the trouble was found to be the contamination of methane sulfonic acid and the use of a new solvent recovered the normal values.

During the run of the routine check, the suppressor

trouble occurred twice. The first new suppressor was installed on November 22, 1995, but had to be replaced with another only four months later (March 13, 1996). The second one has been working well for more than two years. The retrospective analysis discloses the fact that the first suppressor had a kind of problem, ever since it had been installed (see below).

Figs. 4 and 5 show the baselines and their power spectra, respectively, for the period of the second suppressor trouble. The explanation of the first suppressor trouble is omitted because of less information than the second trouble.

The power spectrum of 3/14 is normal and the others suggest a kind of trouble. The anomaly of the spectra (2/8, 2/28, 3/6 and 3/12) are unmistakable. Besides the high values of the criterion in Fig. 1, the pattern of the noise power spectrum is far different from the common  $1/f$  type. This anomalous pattern makes the goodness of fit poor (see the zigzag and smooth lines in Fig. 5).

The power spectrum of 1/9 gives the value of the criterion ( $=0.02$ ) close to the normal one. To readers who are not familiar with noise power spectra, those of 1/9 and 3/14 might look similar. However, we can recognize a knoll around 0.2 Hz over the  $1/f$  pattern which the normal spectrum (3/14) lacks. The knoll had appeared just after the first suppressor

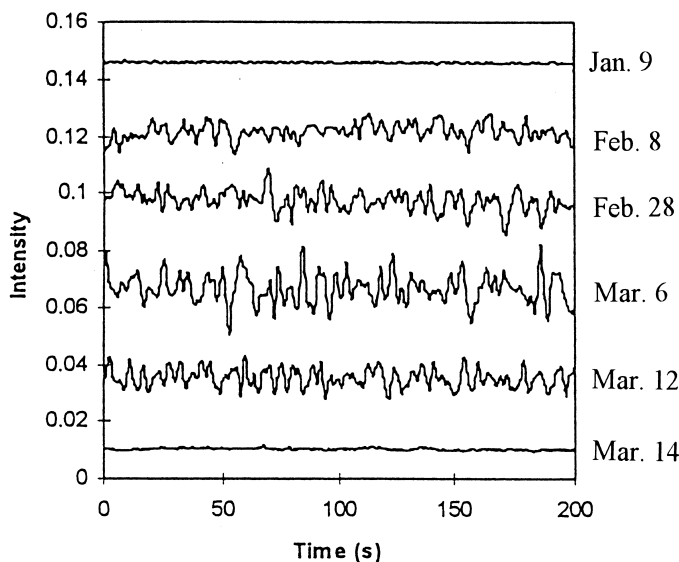


Fig. 4. Baselines in case of suppressor breakdown in 1996.

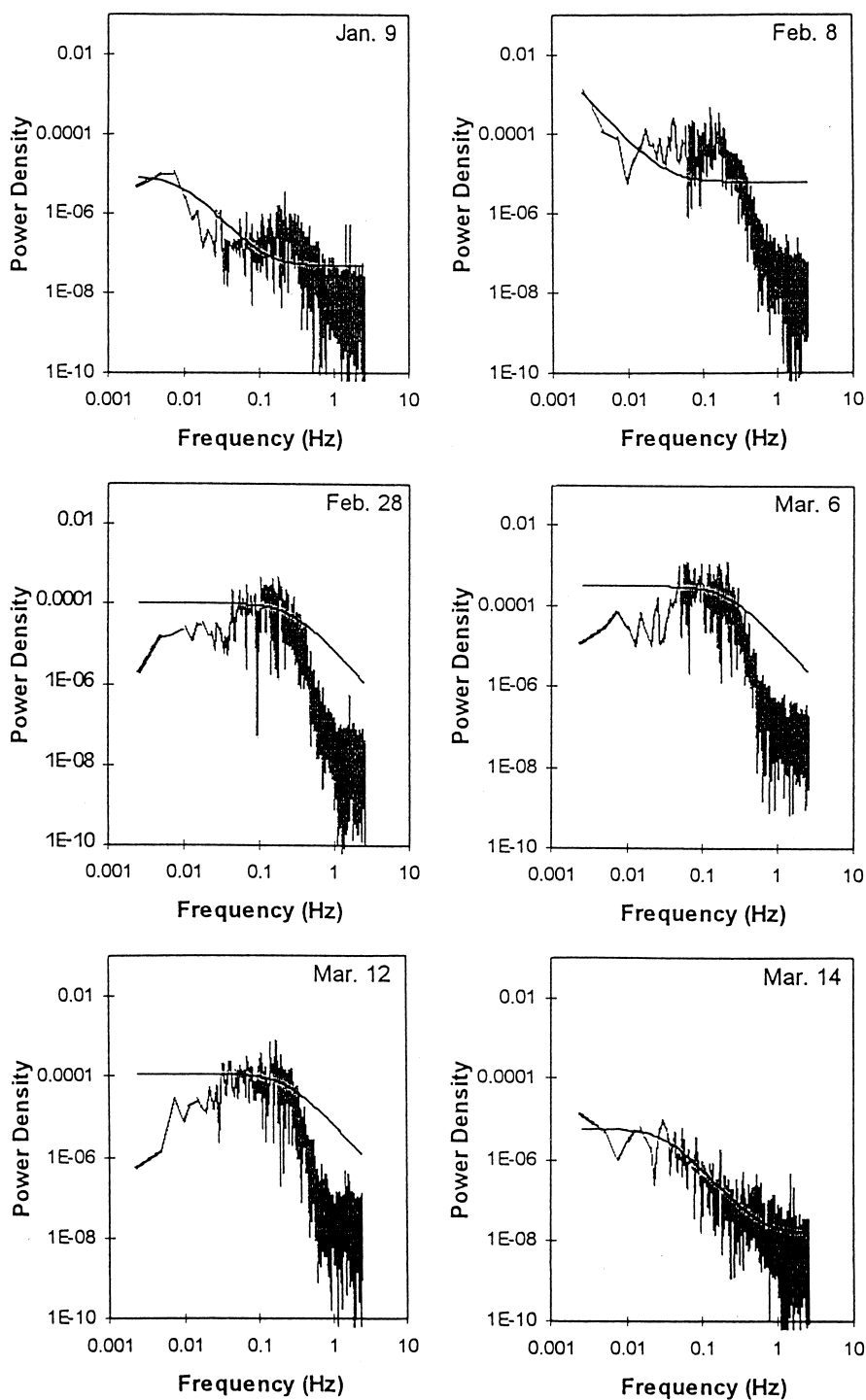


Fig. 5. Power spectra in case of suppressor breakdown in 1996. The power spectra are obtained from the baselines of Fig. 4. Measurement S.D.: 0.012 for 1/9; 0.28 for 2/8; 0.46 for 2/28; 0.61 for 3/6; 0.37 for 3/12; 0.038 for 3/14.

exchange on 11/22 and has not yet done ever since the second exchange on 3/13. That is, the knoll can be an indicator for a poorly manufactured suppressor.

The noise amplitudes of baselines 1/9 and 3/14 have no substantial difference (see Fig. 4) and will not be helpful to examine the quality of the new suppressor. An advantage of the routine check of this paper is that the noise power spectrum can provide more information than the noise amplitudes.

The second suppressor exchange was really carried out on March 13, 1996, more than a month after the high value of the criterion had first been found on February 8 (see Fig. 1). Readers might expect much earlier exchange.

Fig. 6 shows the parts of the chromatograms (baselines) that an analyst actually monitored for the routine check at that time. The analyst could not notice any problem, until the unknown large peaks appeared on the baseline of 3/12. If the baselines were monitored on the expanded scale like Fig. 4 or if the noise power spectra were checked, the earlier finding of the trouble could have been possible. The unknown peak is not used for the calculation of the measurements S.D. shown in Fig. 1.

Generally, the conductivity changes by 2% per 1°C change in temperature and the conductivity change spoils the measurement uncertainty. How-

ever, this would be impossible, as far as the results of Fig. 1 are concerned. The IC system used was placed inside a clean room in an air-conditioned room of a building where the temperature of all the rooms was centrally controlled. The temperature recording said that the room temperature was usually stable within  $\pm 0.5^\circ\text{C}$  fluctuation around  $25^\circ\text{C}$ . We should note that the measurement S.D. was calculated for a peak of ca. 10 s width. If the cycle of the conductivity change was 10 s or less, it would have affected the measurement S.D. more or less. However, it is concluded the temperature change was too small and slow to cause the great change in the measurement S.D. shown in Fig. 1.

In case of the solvent contamination, the absolute value of conductivity was observed to increase and the fluctuation of conductivity around the value also increased as shown in Fig. 1. In the FUMI theory, large fluctuation results in a large measurement S.D., but high conductivity without large fluctuation exerts no influence on the uncertainty (S.D.). Therefore, the bleed of a contaminant from the column or suppressor seems to increase both the conductivity and its fluctuation.

The  $1/f$  noise appearing at the last stage of instrumental measurement results from a large number of sources. However, driving the IC system while eliminating a unit from the system will help identify

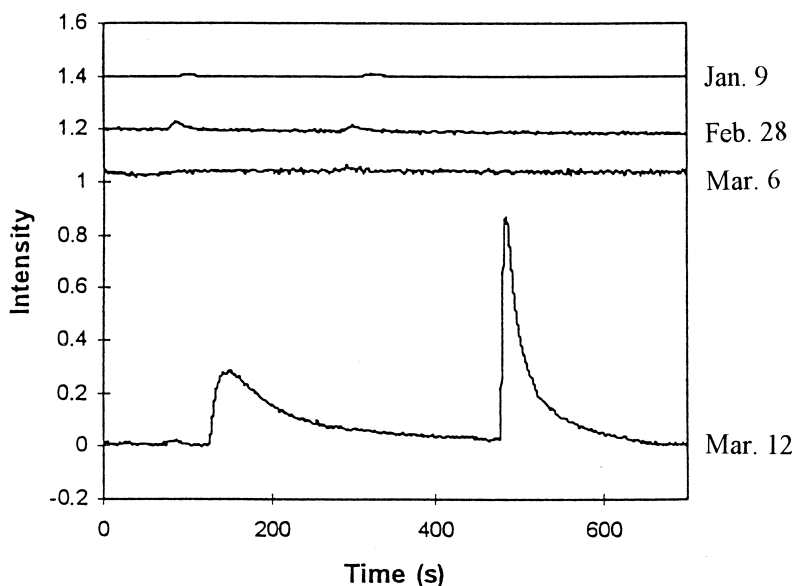


Fig. 6. Parts of chromatograms in case of suppressor breakdown in 1996.

the sources of the measurement uncertainty. If the column is bypassed, the possible error sources such as chemical noise, polarity change and temperature control on the column can be examined. This methodology has been adopted for the study of spectrometry uncertainty by Ingle, Jr. and Crouch [1]. However, the most prominent advantage of this study is the convenience of the trouble detection. The identification of the error sources is beyond the scope of this study.

The retrospective consideration of this study corroborates the advantage of the routine noise check, that is, the early detection of the trouble.

### Acknowledgements

This work was supported by Japan Health Sciences Foundation.

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