

Note

Stability of the electron-capture detector

Use of linear calibration curves referenced to an internal standard for quantitation of trihalomethanes

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Linear calibration curves referenced to an internal standard can be used to minimize the effect of a detector's drift on quantitation. Examples of this approach in the organic analytical literature include: calibration curves used for pesticide analysis by gas chromatography (GC) with electron-capture detection (ECD)¹; calibration curves for routine analysis of purgeable compounds by GC-mass spectrometry². In the latter case, calibration curves were generated at monthly intervals, with new standards made up every three months.

In this paper we describe use of linear calibration curves referenced to an internal standard for quantitation of trihalomethanes (THMs) analyzed by GC-ECD. The electron-capture detector is known to be sensitive to contamination from column bleed, oxygen and electrophilic solvents, not to mention trace contaminants (including water) in samples being analyzed. The effect of oxygen merits particular consideration, in that it *enhances* the sensitivity of the electron-capture detector to THMs^{3,4}. Procedures for cleaning the detector include baking it at 400°C to restore its standing current *versus* frequency response⁵.

Our investigation of regression analysis techniques for THM quantitation was prompted by the relative simplicity of the analysis, combined with a data system programmable in BASIC and the use of an autosampler to minimize the inconvenience of running standards over a range of concentrations. The original program was written in our laboratory over five years ago, although it has been only during the last two years that the program was used extensively enough for an evaluation to be made.

EXPERIMENTAL

Chromatographic analysis

Samples are analyzed for THMs on a Perkin Elmer Sigma 1 gas chromatograph equipped with a Model 4990 autosampler and ⁶³Ni electron-capture detector. Although our instrument configuration includes moisture traps on carrier gases, no oxygen traps are used. THMs are separated on a 1.8 m × 2 mm I.D. column packed

with 80–100 mesh Chromosorb 101, operated isothermally at 165°C, with the injector and detector blocks maintained at 225 and 300°C, respectively. The carrier gas [argon–methane (95:5); 99.999% purity] is supplied at 11 ml/min to the column and at 34 ml/min as make-up to the detector. Typical elution times are 3.21 min for chloroform, 6.15 min for dichlorobromomethane, 9.62 min for 2-bromo-1-chloropropane (the internal standard), 11.17 min for chlorodibromomethane and 21.17 min for bromoform; total run time is 30 min per sample. Standards are prepared in hexane or methanol, using chemicals of reagent-grade purity. For this study, calibration curves based on new standards were generated according to the work load of samples being analyzed: the average interval was 5.0 ± 3.8 weeks.

Data reduction

Quantitative analysis is carried out following injection of a set of standards and samples; results in terms of integrated peak areas are saved in data files in the Sigma 1 memory for later access by the quantitation program, written in BASIC. The original version of the program occupied 570 words of the 6K of RAM in the Sigma 1; modifications to reference standard curves to an internal standard have expanded the program to 1369 words. Coefficients of a linear standard curve are calculated for each of the trihalomethanes injected (3 μ l) as mixed standards at 0.1, 0.2, 0.5, 1.0 and 2.5 mg/l. Values for the correlation coefficient, r^2 , are typically better than 0.999, in agreement with an observation that $r^2 \geq 0.98$ can generally be obtained for chromatographic calibration curves¹. The program then determines THM concentrations in individual samples, after requesting as input the sample file name, the volume of solvent used for extraction, and the sample volume (for granular activated carbon samples). In each sample file, a quality control check is performed on detection of the internal standard (at 10 mg/l), and deviations are flagged in the report.

Sample files are transferred to cassette tape for storage.

RESULTS

Data in Fig. 1 reveal the progressive change in absolute sensitivity of our electron-capture detector over a two-year period. It is also apparent that sensitivity for THMs is reduced when methanol is the solvent instead of hexane. For each of the THMs, and for the internal standard, there is an overall trend of increasing sensitivity: per cent changes for the entire period, relative to initial values, are 114, 97, 92, 96, and 81% for chloroform, dichlorobromomethane, 2-bromo-1-chloropropane, dibromochloromethane and bromoform, respectively. Corresponding rates of increasing sensitivity are therefore 0.88, 0.75, 0.71, 0.74 and 0.62% per week. Thus for each five weeks, detector sensitivity increases an average of 3.7%.

The time span for data in Fig. 1 includes many changes of gas tanks, detector cleanings, several different columns, and many samples analyzed. In retrospect, it is not possible to identify specific causes of the change in detector sensitivity, although traces of oxygen in the carrier gas are suspect. It is of interest that the change in sensitivity can be monitored in time by the repeated analysis of an internal standard at a fixed concentration; this behavior alone could be used as a basis for determining the need to regenerate standard curves, or clean the electron-capture detector if sensitivity decreases.

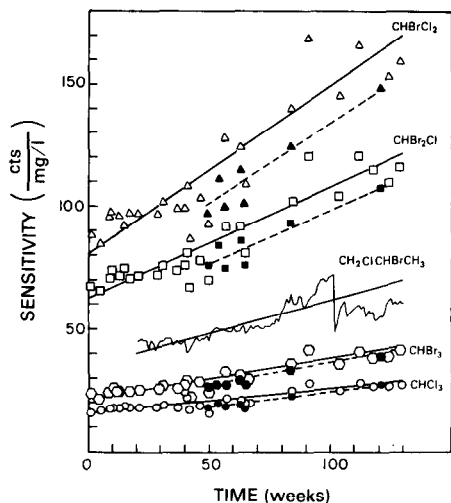


Fig. 1. Time variance of GC-ECD sensitivity [cts/(mg/l)] to the THMs. Open symbols are for THMs in hexane. Closed symbols are for THMs in methanol. Data for the internal standard 2-bromo-1-chloropropane are the average of ECD responses (cts) for 10 mg/l spikes added to all samples analyzed in a particular week. Solid lines represent a linear fit to time dependent data.

The data in Fig. 2 show the advantages of normalizing all standard curve data to an internal standard. Net changes in relative sensitivity for the entire period amount to -4.0 , 12 , 8.8 , and 2.6% for chloroform, dichlorobromomethane, chlorodibromomethane and bromoform respectively. Corresponding rates of change in sensitivity are therefore -0.03 , 0.09 , 0.07 , and 0.02% per week. Since the drift in relative sensitivity is insignificant, requirements on the frequency of regenerating standard curves can be relaxed, as long as quality control checks are routinely made. The relative precision of sensitivity (indicated by dashed lines in Fig. 2) for the re-

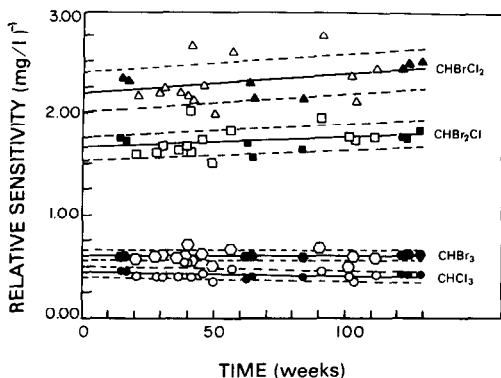


Fig. 2. Time variance of relative GC-ECD sensitivity [$1/(\text{mg/l})$] to THMs, normalized to response to the internal standard 2-bromo-1-chloropropane. Open symbols are for THM sensitivity normalized to week's average response to internal standard (contained in samples but not standards). Closed symbols are for THM sensitivity, with the response to individual compounds normalized to the response to the internal standard (spiked directly into all standards). Solid lines represent a linear fit to time dependent data. Dashed lines represent ± 1 deviation of fitted lines.

spective compounds over a two-year period was 11, 9, 7, and 8%. Thus if relative standard curves are used, it is possible to maintain much tighter controls on their reproducibility than if absolute standard curves are used for individual THMs.

CONCLUSIONS

Calibration curves for the THMs should be normalized to an internal standard (2-bromo-1-chloropropane) to eliminate positive drift in the electron-capture detector's sensitivity with increasing time and use. If this is done, relative sensitivity for the four THMs can be held reproducible to within an average of 9% over a two-year period.

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