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EVALUATION OF A CALIBRATION MARKER SCHEME FOR OPEN TUBULAR COLUMN GAS CHROMATOGRAPHY WITH ON-COLUMN INJECTION AND ELECTRON-CAPTURE DETECTION*

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SUMMARY

A new method of calibration for open tubular column gas chromatography with electron-capture detection is proposed. A homologous series of *n*-alkyl bromides is added to each sample analyzed to provide simultaneously a retention index scale and a method of solute calibration. The detector response to equimolar amounts of *n*-alkyl bromides is constant, permitting a calibration curve to be generated for each sample by adding a series of *n*-alkyl bromides arranged in increasing stepwise molar concentrations. Each solute is then treated as if it were an imaginary *n*-alkyl bromide of some concentration obtained from the experiment and converted to an actual concentration from the relationship between the solute and *n*-alkyl bromide calibration curves, stored in the computer memory. It is shown that for the complete chromatographic system, temperature-programmed retention indices can be reproduced with an average standard deviation of *ca.* 0.35 index units and that the relative error for the calibration method is similar to that obtained by daily solute calibration. The advantages of the new method are that it combines the operation of solute identification by retention index values and multiple solute calibration into a single method, capable of automation. Compared to standard calibration procedures, it is less time-consuming and subject to fewer operator errors.

INTRODUCTION

The electron-capture detector is widely used for the analysis of many environmentally and biomedically important compounds. However, quantitation of multicomponent mixtures with this detector is not as straightforward as for other detectors in routine use. The detector response for a particular substance depends on the type and flow-rate of the carrier and detector make-up gases, the detector temperature, the substance-specific electron-capture coefficient, and the general level of detector contamination[1,2]. For most substances the detector responds in a concentration-de-

* Dedicated to Professor A. Zlatkis on the occasion of his sixtieth birthday.

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pendent manner. Quantitative information is obtained by calibration of the detector for each substance of interest in the mixture chromatographed. Here, an immediate disadvantage of the electron-capture detector emerges, compared to such detectors as the flame ionization detector. For compounds containing several carbon atoms little variation in response factors is observed with the flame ionization detector. A single calibration curve can therefore be used to quantify all components in the mixture, albeit with some loss in accuracy. Response factors for the electron-capture detector are not only unequal for most organic compounds but span several orders of magnitude. Consequently, each substance must have its own calibration curve. Also, as the day-to-day reproducibility of the electron-capture detector response is not as consistent as the flame ionization detector, and calibration must be repeated at frequent intervals to account for the changing conditions under which the detector is operating.

Alternatively, an internal standard of known concentration can be added to each sample being analyzed. The internal standard is able to correct to some extent for changes in detector response and sample injection volume between analyses. Intuitively, the accuracy of the internal standard method should be maximized when the structure, concentration, and retention time of the internal standard closely match those of the substance of interest. This situation is rarely obtained for all components eluted from a capillary column unless only a few components of similar structure are to be determined.

The identification of substances by gas chromatography is usually based on the accurate measurement of retention. The retention index scale devised by Kováts is widely accepted for this purpose[3,4]. On this scale, the retention index of a substance is defined as a value equivalent to 100 times the carbon number of a hypothetical *n*-alkane with the same adjusted retention time. The fixed points on the retention index scale are thus defined by a homologous series of *n*-alkanes injected together with the sample. Since the electron-capture detector shows no significant response to the *n*-alkanes, this method is not suitable for use with it. Retention indices have been determined indirectly by using series- or parallel-coupled flame ionization and electron-capture detectors[5,6]. However, a more elegant solution to this problem is to employ substances responding to the electron-capture detector as the fixed points on the retention index scale. The *n*-alkyl trichloroacetates[7–10] and *n*-alkyl bromides[11] have been used for this purpose. Only the fixed points on the retention index scale are changed, the calculation method remains the same as that proposed by Kováts.

In this paper a novel calibration marker scheme is evaluated for use in open tubular column gas chromatography with electron-capture detection. A homologous series of *n*-alkyl bromides is used to provide simultaneously both a retention index scale and a solute calibration curve for all substances present in the sample. The molar response of the electron-capture detector to the *n*-alkyl bromides is constant, and by arranging for the *n*-alkyl bromides to be present in stepwise increasing concentration, a linear calibration curve results. The "calibration method" and the "error-reduction method" are then used to convert the response data for the substance as an imaginary *n*-alkyl bromide into the actual sample concentration. This transformation requires that the relationship between the substance and *n*-alkyl bromide calibration curves be determined in a preliminary experiment and then stored in the computer.

EXPERIMENTAL

The *n*-alkyl bromides (C_5–C_{18}), bromobenzene, isophorone, chloronaphthalene, *o*-chlorophenol, and *o*-dichlorobenzene were obtained from Aldrich (Milwaukee, WI, U.S.A.). Standard solutions covering the range bromobenzene (8–48 ppb), *o*-dichlorobenzene (0.7–4.0 ppb), isophorone (22–130 ppb) and *o*-chlorophenol (28–170 ppb) were prepared by dilution in pesticide residue grade *n*-hexane (Burdick & Jackson Labs., Muskegon, MI, U.S.A.). The *n*-alkyl bromides were added in stepwise increasing concentration to provide a response with the electron-capture detector covering the range 10,000–60,000 peak area counts.

For chromatography, a Varian 3700 gas chromatograph with a 8-mCi ^{63}Ni pulse-modulated constant-current electron-capture detector was used. The column was a 60 m × 0.32 mm I.D. DB-1 bonded phase (1 μm film thickness) fused-silica capillary column (J & W Scientific, Rancho Cardova, CA, U.S.A.). Separations were carried out with a temperature program from 60 to 200°C at 2°C min^{-1} and a helium carrier gas flow-rate of 1.5 ml min^{-1}. The carrier gas was purified by passage through a Go-Getter (Alltech, Deerfield, IL, U.S.A.). Oxygen-free nitrogen at a flow-rate of 40 ml min^{-1}, purified by passage through an Oxysorb trap and a molecular sieve trap, was used as the detector make-up gas. The detector temperature was maintained at 400°C. The chromatograms were recorded with a Spectra Physics 4100 computing integrator (Spectra Physics, San Jose, CA, U.S.A.). Additional calculations were performed on an Eclipse S/310 minicomputer (Data General, Westboro, MA, U.S.A.)

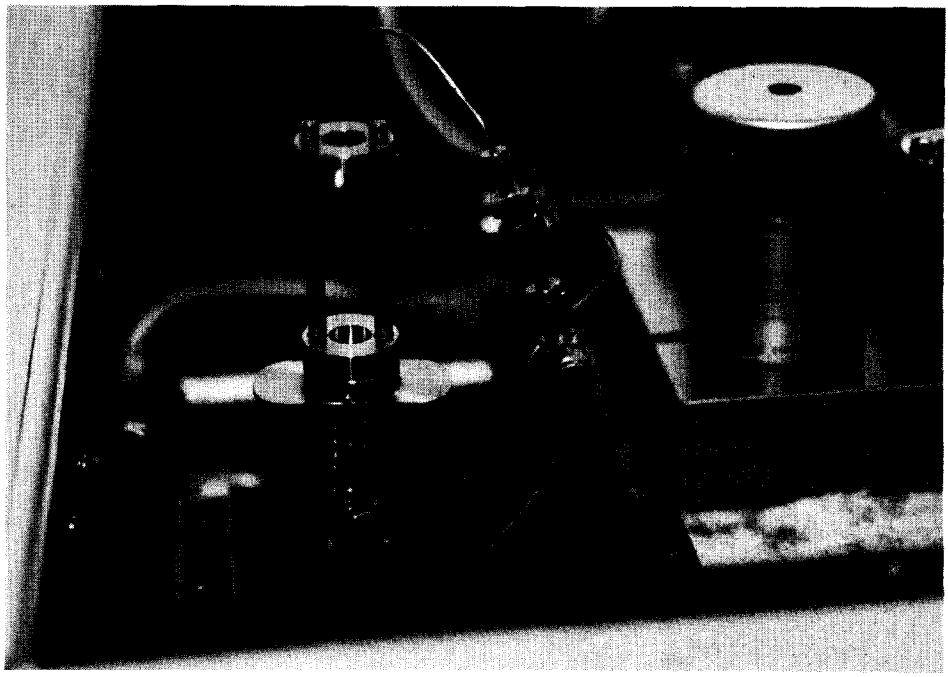

Fig. 1. On-column injector, mounted on the Varian 3700 gas chromatograph.

with programs written by the authors in FORTRAN IV. A copy of the programs and all the experimental data collected during this study is available[12].

All samples were injected with a Hamilton 701 syringe having a 13 cm (32 gauge) fixed stainless-steel needle (Anspec, Ann Arbor, MI, U.S.A.) into a laboratory-built on-column injector. The capillary inlet split injector was removed and replaced with the on-column injector. The latter was designed to use the same retaining screws as the split injector. The on-column injector (see Figs. 1 and 2) was based on a design proposed by Zlatkis and co-workers[13–16] and modified for stopped-flow

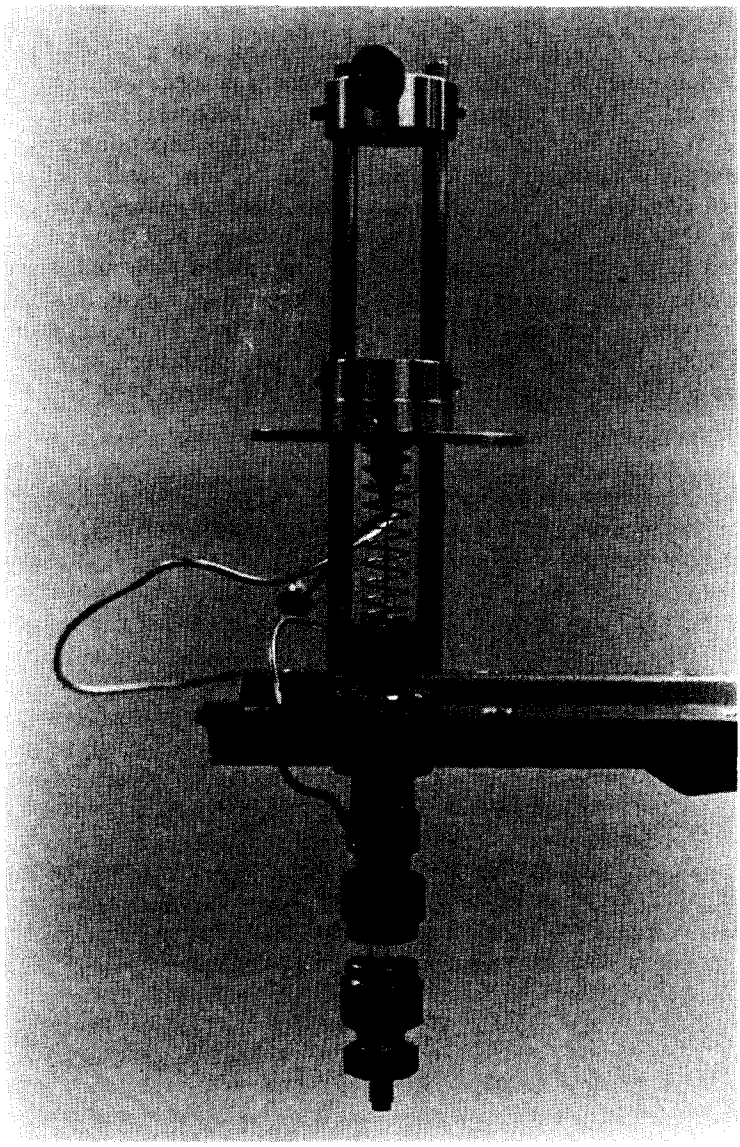

Fig. 2. Assembled view of on-column injector.

injection using the existing pneumatics of the capillary split injector of the Varian 3700[17]. The on-column injector was a septum injector with a wide-bore guide needle to protect and transport the syringe needle through the septum and a glass constriction tube to guide the sample syringe needle into the capillary column. The optimum conditions for injection were determined to be:

(1) The injection sequence should follow the order stop flow, insert needle into column, make injection, reactivate flow, and remove syringe needle.

(2) The sample volume should be not larger than 2 μl, and a solvent flush of 1 μl should be used to ensure that all of the sample is pushed out of the syringe.

(3) It is important that, after the carrier gas flow is stopped by diversion from the column through the original solenoid-controller split line (Fig. 1) or by closing the carrier gas flow control valve, the column is de-pressurised by penetrating the septum with the guide needle for about 5 sec prior to inserting the sample syringe needle.

(4) The plunger of the sample syringe should be depressed smoothly and rapidly.

(5) The column oven temperature should be within $\pm$ 10°C of the boiling point of the sample solvent.

RESULTS AND DISCUSSION

The calibration marker scheme was devised for the simultaneous production of a retention index scale and solute calibration method for the electron-capture detector. At the outset it should be noted that the performance of a total system is involved. Variations in the data can be expected to arise not only from the detector, but also from inadequacies in the temperature and pneumatic components of the gas chromatograph, from adsorption on the column, from unreliability of the integrating device, and from the performance of the injector. The gas chromatograph, column, and computing integrator are commercial products, which were not optimized for this work.

Quantitative sample introduction for mixtures of wide boiling point and concentration differences has long been recognized as a problem in open tubular column gas chromatography. The recent introduction of on-column sampling devices finally seems to have solved most of these problems. Sample discrimination and decomposition due to thermal or catalytic effects are largely eliminated. In this study an on-column injector, operated in the stopped-flow mode was used. Compared to continuous-flow operation, stopped-flow has the advantages of sharpening later eluted peaks and eliminating peak splitting[17]. Peak splitting in particular, can be a problem as it prevents accurate electronic integration of peak areas. In an independent study in which the flame ionization detector was used, the reproducibility of injection in the stopped-flow mode was established as *ca.* 2.7% R.S.D. for sample components spanning a wide range of concentrations and volatilities[17].

Retention index calibration

Two modifications were made of the retention index scale devised by Kováts to make it compatible with the requirements of the electron-capture detector and also for the determination of samples of a wide boiling point range. First, the *n*-alkyl

bromides were selected as the fixed points on the new retention index scale. Secondly, the retention indices were measured by using a linear temperature program and eqn. 1 for the calculation[18,19].

$$I = 100\left[\frac{T_{R(S)} - T_{R(Z)}}{T_{R(Z+1)} - T_{R(Z)}} + Z\right] \quad (1)$$

where I = retention index of substance S under temperature programmed conditions; $T_{R(S)}$ = time required for elution of substance S; $T_{R(Z)}$ = time required for elution of the n-alkyl bromide with Z carbon atoms, emerging before substance S; $T_{R(Z+1)}$ = time required for elution of the n-alkyl bromide with $Z + 1$ carbon atoms, emerging after substance S.

The column temperature at the time of elution may also be substituted into eqn. 1 for the elution time. The latter is more convenient, as the information is printed on the chromatogram by the integrator.

Typical values for retention indices are presented in Table I. Each entry is for a single chromatogram, obtained one week apart, and selected at random from the complete data base. As can be seen, the reproducibility of the retention indices is very good with a standard deviation in the range of 0.15–0.65 retention index units. The largest change was observed in the value of isophorone, which shows a trend towards a higher value with time, perhaps indicating a change in column performance to which isophorone was most influenced. A typical chromatogram for a calibration run is shown in Fig. 3.

Solute calibration

For a homologous series of n-alkyl bromides the ECD response is proportional to the concentration of bromide ions generated by electron-capture and is independent of the length of the alkyl chain (possible exceptions might be the first few mem-

TABLE I

REPRODUCIBILITY OF RETENTION INDICES UNDER TEMPERATURE PROGRAMMED CONDITIONS WITH n-ALKYL BROMIDE AS THE FIXED POINTS

	Bromobenzene	*Chlorophenol*	*o-Dichlorobenzene*	*Isophorone*	*Chloronaphthalene*
	595.80	651.64	694.56	771.04	1032.84
	595.87	651.54	694.64	771.25	1033.06
	595.68	651.47	694.32	771.33	1032.79
	595.69	651.27	694.70	771.09	1032.31
	595.01	651.37	694.58	771.80	1032.97
	595.02	651.80	694.78	772.45	1033.65
	596.07	651.93	694.71	772.65	1033.64
	595.68	651.46	694.35	772.65	1033.73
	595.67	651.76	694.60	772.08	1033.00
	595.08	651.61	694.57	772.33	1033.50
$\bar{X}$	595.56	651.59	694.58	771.87	1033.15
S	0.38	0.20	0.15	0.65	0.46
R.S.D. (%)	0.06	0.03	0.02	0.08	0.04

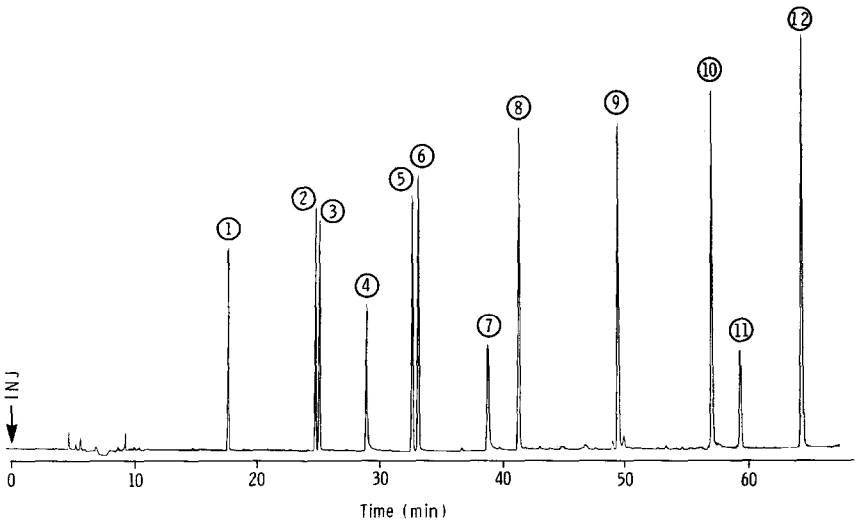

Fig. 3. Typical chromatogram of a standard mixture. Peak assignments: 1 = C_5Br; 2 = bromobenzene; 3 = C_6Br; 4 = *o*-chlorophenol; 5 = *o*-dichlorobenzene; 6 = C_7Br; 7 = isophorone; 8 = C_8Br; 9 = C_9Br; 10 = $C_{10}Br$; 11 = chloronaphthalene; and 12 = $C_{11}Br$.

bers of the series). Based on this premise, two new methods of solute calibration have been devised. These methods are termed the "calibration method" and the "error-reduction method". A description of both methods is given below.

For the calibration method, it is necessary to establish the relationship between the calibration curve for the calibration markers (Fig. 4, curve 1) and the sample (Fig. 4, curve 2). The calibration curve for the calibration markers is obtained from a series of *n*-alkyl bromides added to the sample to provide a linear increase in the detector response to each *n*-alkyl bromide of increasing molecular weight added. The

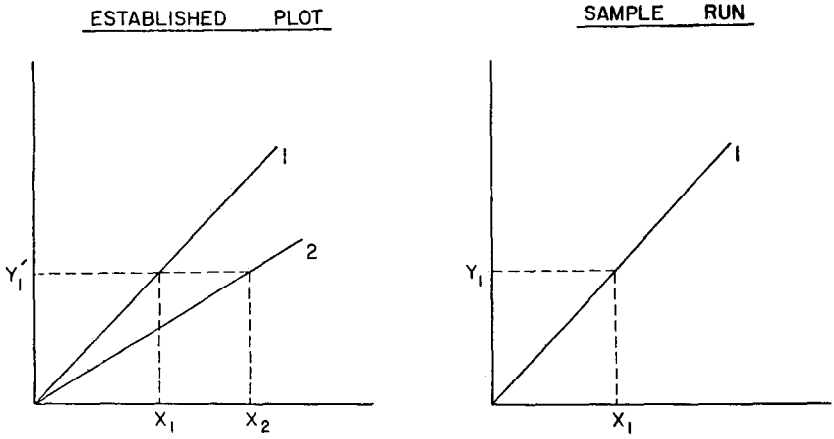

Fig. 4. Plot of detector response against concentration for the "calibration method". Y_1 = solute response on the *n*-alkyl bromide calibration curve equivalent to an *n*-alkyl bromide concentration X_1. Y_1' = projection of X_1 on the established plot giving a corrected solute concentration X_2.

calibration curve can be imaginary or normalized to a fixed concentration of one of the *n*-alkyl bromides; this is unimportant as long as the relationship is linear. Once a suitable number and concentration range of *n*-alkyl bromides have been selected, they should remain unchanged in all further experiments. A standard calibration curve for the substance of interest is obtained in the usual way. The two calibration curves, one for the calibration markers and the other for the substance of interest are then stored in the computer and form the data base for all subsequent calibration runs. The two calibration curves can be represented by the equation of a straight line $Y = MX + C$, where Y = detector response (peak area), M = gradient of the calibration curve, X = concentration term, and C = intercept (ideally set equal to zero). The corrected concentration of the substance of interest can be related to the response of the detector to that substance in the sample analyzed by eqn. 2.

$$X_2 = M_1X_1(M_2)^{-1} + (C_1 - C_2)(M_2)^{-1} \quad (2)$$

where X_2 = unknown concentration of test substance; M_1 = slope of the *n*-alkyl bromide calibration curve; X_1 = concentration of *n*-alkyl bromide having the same area response as X_2; M_2 = slope of the calibration curve for X_2 determined in a preliminary experiment.

Expressed in words, the calibration method works as follows. The substance to be determined is injected together with a mixture of calibration markers. The chromatogram obtained after normal data handling reproduces the calibration curve for the calibration markers (Fig. 4, curve 1), and provides a retention index value and an area response value for the substance of interest. The detector response to this substance is then treated as if it were an imaginary *n*-alkyl bromide found to have a concentration X_1 from the *n*-alkyl bromide calibration curve. This value of X_1 is then used to calculate X_2 by using eqn. 2 and the established data stored in the computer.

In the "error-reduction method" (Fig. 5), the observed response for the sub-

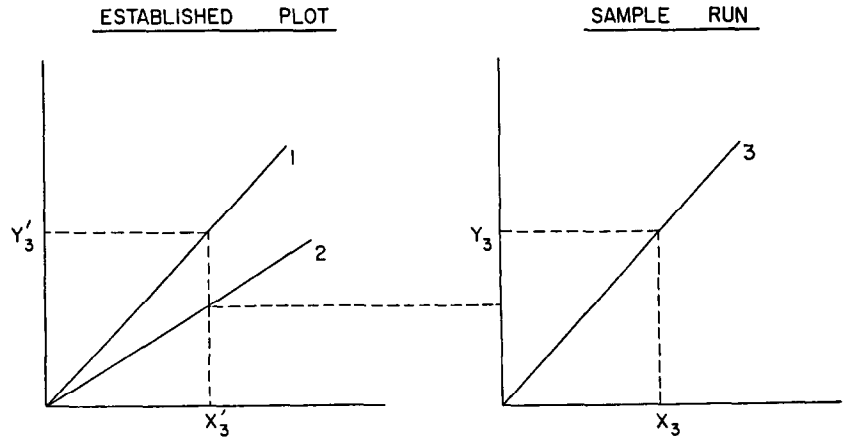

Fig. 5. Plot of detector response against concentration for the "error-reduction method". Y_3 is the solute response on the *n*-alkyl bromide calibration curve corresponding to an *n*-alkyl bromide concentration X_3. Y'_3 is the solute response on the *n*-alkyl bromide calibration curve 1.

stance of interest is used to calculate its uncorrected concentration X_3 from the calibration curve 3 (as described for the calibration method). If the substance of interest had been an imaginary *n*-alkyl bromide of concentration X_3, it would generate a response Y_3 on curve 3 (sample run) and Y_3' on curve 1, the established plot. The ratio Y_3'/Y_3 is then used to correct for the response/concentration differences between the two calibration curves, 1 and 3. The corrected value for the response Y_3'', not shown in Fig. 5, is then used to calculate a corrected concentration X_4 for the substance of interest by using calibration curve 2, as described previously. The "error-reduction method" assumes that the small change in the detector response characteristics represented by the small differences between curves 1 and 3 in Fig. 5 faithfully mirror the expected change in the detector response to the sample. This should be true for substances that are similar to the *n*-alkyl bromides in electron-capture properties but perhaps not so for substances with different response characteristics.

To evaluate the different calibration methods a series of standard solutions was prepared, containing various concentrations of bromobenzene, *o*-dichlorobenzene, isophorone, and *o*-chlorophenol along with the *n*-alkyl bromides C_5 through C_{11}. The concentration of *n*-alkyl bromides was the same in all standards. These standard solutions were analyzed at frequent intervals over a three-month period, including times when the instrument was used for other purposes to simulate normal laboratory use. Here we will summarize the conclusions reached from interpreting these data; the complete raw data and computer programs employed for the study are available elsewhere[12].

A typical computer print-out for one substance in a single chromatographic run is shown in Fig. 6. The solution number and experiment number, as well as the solute to which the data pertains are listed on the first line. The slope, *Y*-intercept, and correlation coefficient (R^2) of the line, produced by the *n*-alkyl bromides in the particular experiment is listed next, followed by the *X* value obtained for the con-

```
Run 4 3B Bromobenzene

Slope = 6443.9        Y-intercept = 9805.6          Corr = 0.9991

Error Reduction Method = 4.3891 . . . . . %Error = -0.3
Calibration Method = 4.3665 . . . . . %Error = -0.8

The corrected value using single bromide #5  = 4.3999        %Error =  -0.0
The corrected value using single bromide #6  = 4.3105        %Error =  -2.0
The corrected value using single bromide #7  = 4.3685        %Error =  -0.8
The corrected value using single bromide #8  = 4.3604        %Error =  -0.9
The corrected value using single bromide #9  = 4.3604        %Error =  -0.9
The corrected value using single bromide #10 = 4.3533        %Error =  -1.1
The corrected value using single bromide #11 = 4.4803        %Error =   1.8

The corrected baseline calib. C5  bromide = 1.2775          %Error = 16.1
The corrected baseline erred. C5  bromide = 1.2759          %Error = 16.0

The corrected baseline calib. C8  bromide = 1.2775          %Error = -1.7
The corrected baseline erred. C8  bromide = 1.2759          %Error =  0.0

The corrected baseline calib. C11 bromide = 1.2775          %Error =  0.0
The corrected baseline erred. C11 bromide = 1.2759          %Error =  0.0

The uncorrected value from solute line = 4.7374     %Error = 7.7
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Fig. 6. Typical computer print-out, summarizing the data obtained from a single standard in one chromatogram.

centration of the solute analyzed (bromobenzene in this particular example) by both the calibration and the error-reduction methods, and the percent relative error obtained with each method. Listed next is the percent error obtained for the solute concentration if the *n*-alkyl bromides are used by themselves as a single-point calibration method. Since the calibration and error-reduction methods should work best for compounds similar to alkyl bromides, relative error values were determined for the C_5, C_8 and C_{11} *n*-alkyl bromides when the other bromides were used to correct for their concentrations by using the calibration and error reduction methods. These values would be expected to be "baseline" values in that this is probably as low an error as one could hope to obtain with the techniques investigated. Finally, the *X*-value and the relative error value obtained by calculating the solute concentration

TABLE II

COMPARISON OF CALIBRATION METHODS BY USING DATA OBTAINED CLOSE TO THE TIME THE DATA BASE WAS ESTABLISHED

Solute	*Concentration (ppb)*	*Amount injected (pg)*	*Relative percent error (average of 3 determinations)*		
			Solute calibration	*Error-reduction method*	*Calibration method*
Bromobenzene	8	11	4.5	8.2	13.5
	16	21	8.9	9.7	8.7
	24	32	4.5	5.4	5.1
	32	43	14.3	3.6	3.1
	40	54	14.2	4.0	3.4
	48	64	8.8	4.9	5.1
		$\bar{X}$ =	9.2	6.0	6.5
o-Dichlorobenzene	0.7	0.9	4.8	9.8	12.7
	1.4	1.8	8.6	7.6	7.5
	2.1	2.7	7.3	3.4	2.1
	2.8	3.6	8.6	2.4	2.3
	3.5	4.5	8.9	3.2	3.2
	4.2	5.4	12.3	1.9	1.8
		$\bar{X}$ =	8.4	4.7	4.9
Isophorone	22	29	41.8	45.9	55.2
	44	57	15.5	14.4	16.3
	66	86	14.8	10.5	8.0
	88	114	22.8	1.5	3.8
	110	143	16.9	5.9	4.8
	132	172	9.4	6.4	5.2
		$\bar{X}$ =	20.2	14.1	15.6
Chlorophenol	22	29	28.5	31.2	39.7
	44	57	17.9	16.6	18.1
	66	86	15.5	11.8	9.9
	88	114	28.2	12.1	13.5
	110	143	10.4	15.5	14.7
	132	172	15.7	10.9	12.2
		$\bar{X}$ =	17.7	16.3	18.0

from the original solute calibration curve used to establish the data base for the calibration and error-reduction method is listed.

The trends in the data obtained can be discussed by comparing the results obtained relatively close in time to the data that were used to generate the established plots and the original data base with data obtained several weeks later. Tables II and III list the compounds analyzed, the concentration of each solute present in each solution, as well as the amount of sample injected into the column. Each entry in the tables represents an average of three experiments. For data obtained near the time the data were established, the solute calibration curve, "calibration method", and the "error reduction method" all show acceptable precision and accuracy for concentrations in the trace level range. The "calibration method" and the "error-reduc-

TABLE III

COMPARISON OF CALIBRATION METHODS BY USING DATA OBTAINED SEVERAL WEEKS AFTER THE DATA BASE WAS ESTABLISHED

Solute	*Concentration (ppb)*	*Amount injected (pg)*	*Relative percent error (average of 3 determinations)*		
			Solute calibration	*Error-reduction method*	*Calibration method*
Bromobenzene	8	11	31.4	8.1	6.3
	16	21	37.1	6.3	5.9
	24	32	30.3	13.0	11.9
	32	43	31.9	7.0	6.8
	40	54	28.7	7.1	6.6
	48	64	35.2	18.2	18.3
			$\bar{X}$ = 32.4	10.0	9.3
o-Dichlorobenzene	0.7	0.9	34.6	9.2	5.7
	1.4	1.8	36.6	4.7	6.5
	2.1	2.7	29.4	11.0	11.8
	2.8	3.6	34.7	9.8	11.1
	3.5	4.5	32.4	11.4	10.9
	4.2	5.4	32.5	14.6	15.7
			$\bar{X}$ = 33.4	10.1	10.2
Isophorone	22	29	60.3	8.2	14.4
	44	57	56.7	30.6	31.1
	66	86	29.7	16.5	19.2
	88	114	46.0	27.8	25.0
	110	143	48.7	23.2	18.0
	132	172	51.7	34.9	33.4
			$\bar{X}$ = 48.9	24.0	23.5
Chlorophenol	22	29	33.2	6.4	2.3
	44	57	42.1	24.6	20.9
	66	86	28.3	16.8	15.8
	88	114	43.3	29.6	27.0
	110	143	48.4	28.8	18.0
	132	172	48.1	34.8	33.2
			$\bar{X}$ = 40.6	23.5	19.5

tion method" provide concentration values that are marginally more accurate than those obtained by using the solute calibration curve but the improvement is really quite small. The value of the calibration and error-reduction methods becomes evident when Table III is examined, representing data obtained several weeks after the original data base was established. When the original solute calibration curve is used, the precision is found to be quite low, while the "calibration method" and "error reduction method" shows only a moderate change in precision from the values given in Table II. In fact, the calibration and error-reduction methods reduce the error obtained from data obtained several weeks after the original data base was established to levels comparable to those obtained by using conventional solute line calibration on a daily basis. The accuracy and precision of the calibration methods is greatest for bromobenzene, which is the solute most similar to the *n*-alkyl bromides themselves and, being relatively nonpolar, presumably the least influenced by changes in column activity during the time the measurements were made.

Analysis of the individual methods does not suggest any improvement in the accuracy of the data from the "error-reduction method". Although the "error-reduction method" provides an absolute value for the solute concentration that is different from that obtained for the "calibration method", the values obtained are statistically no more accurate or precise than those obtained by the "calibration method". As the "calibration method" is more easily programmed and faster to execute, it is the preferred method.

CONCLUSIONS

The most important aspect as far as quantitative analysis with open-tubular columns and electron-capture detection is concerned is that the data obtained on a one-time basis can be used to calibrate data obtained several weeks later and that the need for daily standardization is thereby eliminated. Also, all the calculations discussed in this paper could be executed on a chromatographic data terminal supplied with many modern instruments. Although not undertaken during this study, it should be entirely feasible to construct an automated instrument for routine analysis where peaks are identified from a library of retention indicies, the appropriate solute calibration curve is searched for, and the concentration of the identified solute is printed out by using the "calibration method". This should be considered the goal toward which our continuing studies are directed.

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