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Welcome to the October 1996 issue of the Customs Laboratory Bulletin! This is the second and final issue for this year.

The Customs Laboratory Bulletin is normally published in January, April, July and October of each year, provided that we receive a sufficient number of articles for publication from you, our readers. If we are to regain and maintain a quarterly publication schedule, we need your help.

The Customs Laboratory Bulletin is looking for articles dealing with intriguing samples, innovative methods of analysis, and other topics of interest to the Customs and related laboratory fields. Our articles are peer-reviewed prior to publication and range in length from short notes to full length reports on major research projects. Our primary focus is on analytical problems encountered by Customs chemists and analysts worldwide.

Instructions for preparing articles for submission were published in the last issue. For further information on submitting an article, to request a subscription, or to share comments and suggestions on how the Customs Laboratory Bulletin could better serve your needs, please contact the Editor at the following address:

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## MEASUREMENT OF FLUORIDE IN TOOTHPASTE

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## INTRODUCTION

Samples of toothpaste have occasionally surfaced in the New York Laboratory for quantitation of fluoride content. Although it is not a tariff problem, there are FDA regulations on the amount of fluoride that toothpaste should contain. The FDA Compliance Department lists fluorinated toothpaste as containing 0.22%-0.24% sodium fluoride or 0.4% stannous fluoride, or 0.76% sodium monofluorophosphate, by weight. The sample used in the following experiment was labeled to contain sodium monofluorophosphate of unknown concentration. The possible problems in analyzing toothpaste include the solubility of the sample and the sample matrix. The quantitation of fluoride is also complicated by possible mixtures of stannous fluoride and sodium monofluorophosphate. The analytical methods available in the United States Pharmacopeia XXII (U.S.P.) and the "National Bureau of Standards Certificate of Analysis for Standard Reference Material 79a Fluorspar" were evaluated and adapted for the analysis of toothpaste.

The U.S.P. method for **Sodium Fluoride** is intended for assays of 98% to 102%. The assay procedure requires a fresh ferric chloride solution which is standardized by titrating with 0.1 N thiosulfate. The NaF sample is titrated with the  $\text{FeCl}_3$  solution. This procedure is time consuming and is written to determine the fluoride concentration of 98% sodium fluoride. The amount of fluoride in toothpaste is significantly less than 98%.

The U.S.P. method for **Sodium Fluoride Oral Solution** has a criterion of "90-110% of the labeled amount of NaF." The assay procedure requires a buffer composed of (1,2-cyclohexylene dinitrilo)tetraacetic acid, glacial acetic acid, sodium chloride and sodium hydroxide. Standards of 190 ug/ml to 1.9 ug/ml are recommended. The potential in mV is measured with a fluoride ion specific electrode and a calomel reference electrode. A plot of the log of fluoride ion concentration vs. potential is used as a calibration curve to determine the sample concentration. Based

on the speculated fluoride concentration of 1mg/50ml, this procedure appears to be more appropriate for the determination of fluoride in toothpaste.

The method for determination of calcium fluoride in fluorspar, addressed in the National Bureau of Standards Certificate of Analysis, involves a lengthy sample preparation procedure because of the physical nature of fluorspar (natural calcium fluoride containing 85-98% calcium fluoride depending on the grade), but requires similar procedures, solutions and equipment for the calibration curve and data measurement.

## EXPERIMENTAL

### Equipment/Reagents

1. A commercial buffer manufactured by Corning (FAD - Fluoride Analysis Diluent) is used. Other commercially available buffers for fluoride ion analysis are also available. Corning FAD is used 1:1 as an ionic strength adjustor and buffer. It contains the ingredients listed in the U.S.P. procedure for Sodium Fluoride Oral Solution.
2. The standards are made from a commercially available standard - Corning Fluoride standard 100 ppm.
3. An Orion Model 96-09 fluoride ion specific combination electrode is used to measure the potential.
4. A stirring plate and a number of stirring bars and magnetic stirrers are necessary to homogenize the solution.
5. The Corning pH/eV meter 120 is used to measure the potential.
6. Distilled/deionized water (DW) should be used to minimize the effects of other ions and of fluoride already added to the water.
7. Plastic beakers and volumetric flasks, and glass pipets are used for dilutions and transfers.

### Slope

Specific ion electrodes tend to have a limited life and should be tested after they have not been used for a while. The "slope" of the Orion electrode is determined as per the instructions in the Orion instruction manual.

### Standard Calibration Curve

An aliquot of a 100ppm fluoride solution is quantitatively transferred to a plastic 100ml volumetric flask, and diluted to the mark with deionized water and buffer solution as follows:

Table I Fluoride Standards Potential Measurements

	100 ppm F <sup>-</sup> (ml)	Deionized Water (ml)	Buffer (ml)	Potential (mV)
1.	1	49	50	84
2.	5	45	50	46
3.	10	40	50	28
4.	25	25	50	5

After the solutions are transferred to plastic beakers and homogenized with magnetic stirbars, the potentials are recorded. A calibration curve is plotted from the potentials vs. the log of the fluoride concentration.

### Sample Preparation

This study involved a single toothpaste sample prepared in triplicate. Each of the replicates was prepared as follows. Approximately one gram of sample toothpaste is weighed into a plastic beaker. 50ml FAD buffer is added. The sample is stirred using magnetic stirring bars until the solution is apparently homogenized. The solution is quantitatively transferred to a plastic 100ml volumetric flask and diluted to the mark with deionized water. The solution is returned to the plastic beaker and the potential is recorded after the reading has stabilized.

Normally, to compensate for the effect of sample matrix on analyte response, a standard and a blank with a similar matrix are used. But in this case, a known toothpaste without fluoride is unavailable, and the toothpaste matrix is comprised of various substances in unknown amounts. Instead, in order to test for the effect of the matrix, a sample was spiked with a known fluoride amount, and the observed increase in fluoride concentration was compared with that calculated.

## RESULTS AND DISCUSSION

A spreadsheet program (EXCEL) is used to graph the standard data and to calculate a best fit line using linear regression. The potential is plotted against the log of the fluoride ion concentration.

GRAPH:

STANDARD CALIBRATION CURVE

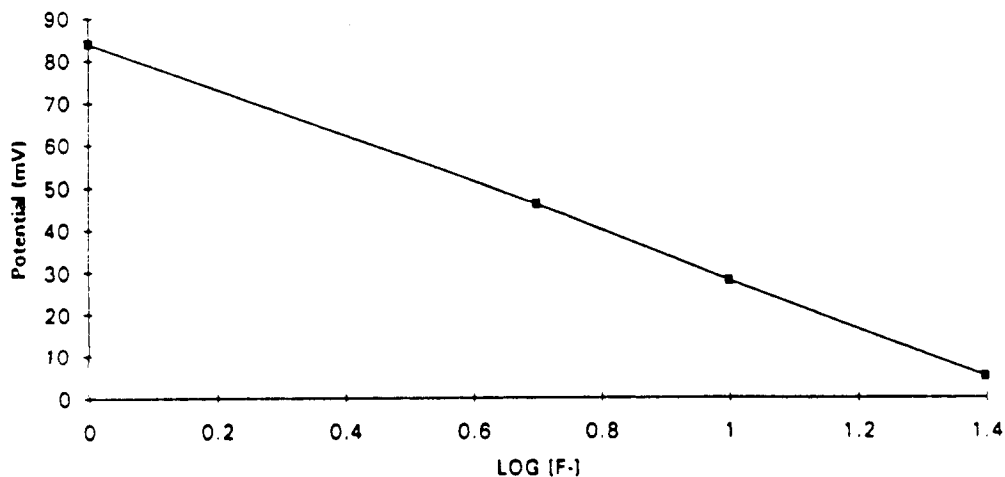


Table II Fluoride Standards Calculated Concentrations

Standards		Potential (mV)	Calculated [F <sup>-</sup> ] (ppm)
[F <sup>-</sup> ] (ppm)	LOG [F <sup>-</sup> ]		
25	1.39794	5	25.51925
10	1	28	9.99665
5	0.69897	46	4.8009
1	0	84	1.02062

Regression results:

The equation of the best line fit represented by the slope-intercept formula ( $y = mx + b$ ) is:

$$y = -56.50919x + 84.50097$$

R-squared, a measure of the linearity of the data, is 0.99955, 1 being a perfect fit.

By substituting the potential (y), the log of the fluoride ion concentration (x) can be found. The antilog will yield the concentration of fluoride ion in the sample solution as ppm.

The percent fluoride in the toothpaste by weight can be determined by the following equation:

$$\%F = [C(\text{ppm}) * V_f(\text{ml}) * 10^{-6} / \text{Sample Wt. (g)}] * 100$$

C(ppm) = F<sup>-</sup> concentration in ppm (determined by experiment)

V<sub>f</sub>(ml) = final volume of analytical solution in ml (100ml)

10<sup>-6</sup> = factor to convert from micrograms to grams

100 = converts fraction to percentage

Table III Sample Calculations and Results

Sample	Sample Weight (g)	Potential (mV)	Calculated [F <sup>-</sup> ] (ppm)	%F <sup>-</sup> in sample	%MFP in sample
1	1.1681	46	4.80089	.04109	.31129
2	1.0209	48	4.42517	.0433	.32803
3a	1.0186	49	4.24848	.04171	.31598
				Standard Deviation	0.008635
3b	3a + 1ml	44	5.20852		



To determine whether the matrix affects the calibration curve, a spiked sample (3b) is compared to the original sample (3a). The spiked sample is the original sample with 1 ml of 100 ppm  $F^-$  solution added. The expected increase in concentration from the spike is 0.9901 ppm based on a volume of 101 ml from the addition of 1 ml 100 ppm  $F^-$  to 100 ml sample solution. Applying a volume of 101 ml to the original sample concentration of 4.24848 ppm yields a concentration of 4.20642 ppm. The total concentration of the spiked sample, calculated from the linear regression, is 5.20852 ppm. The difference between the spiked and unspiked calculated results is 1.00210 ppm compared to theoretical 0.99009 ppm. The two values have a difference of 0.01201 ppm, or approximately 1.2%. The small error can be considered negligible and may be due to experimental error.

If the fluoride is present in toothpaste in the form of sodium monofluorophosphate (MFP,  $Na_2PO_3F$ ), then to compare the experimental concentration of fluoride to the concentration of MFP labeled on the tube or box, the fraction of fluoride in MFP must be calculated. The molecular weight of MFP is 144 and the atomic weight of fluoride is 19.

$$\text{Fraction of fluoride in MFP: } \frac{AW F^-}{MW MFP} = \frac{19}{144} = .132$$

The final part in the analysis is to divide the concentration of fluoride in the sample by the fraction of fluoride in MFP to yield the concentration of MFP in the sample.

$$\%MFP = \% F^- / 0.132$$

Fluoride is present in toothpaste normally as sodium monofluorophosphate. The sample was also ashed and analyzed by emission spectrometry for cations. No trace of tin from stannous fluoride was found.

## CONCLUSIONS

The calibration curve of potential vs. log of fluoride concentration has been shown to be valid using linear regression. The sample matrix does not appear to affect the measurement of fluoride ion as indicated by the spiked samples. This procedure was developed as an exercise in adapting published methods for different applications.

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2. Orion Model 94-09, 96-09 Fluoride/Combination Fluoride Electrodes Instruction Manual, Orion Research Incorporated, Boston, Massachusetts, 1991, pp.5,6,10-12.
3. "National Bureau of Standards Certificate of Analysis Standard for Reference Material 79a Fluorspar"

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**ETHYLENE/VINYL ACETATE COPOLYMERS (E/VAC) - FOURIER  
TRANSFORM INFRARED SPECTROMETRIC METHOD FOR  
DETERMINATION OF VINYL ACETATE CONTENT****Slavomir Falicki, Ph.D.**

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**INTRODUCTION**

The Harmonized Commodity Description and Coding System classifies copolymers according to provisions specified in Note 4 and Subheading Note 1 to Chapter 39. Note 4 defines copolymers as all polymers in which no single monomer contributes 95% or more by weight to the total polymer content. On the other hand, those polymers in which one monomer contributes more than 95% are considered as homopolymers. In border-line situations, it is difficult to decide whether an analyzed product is a copolymer or a homopolymer. Such cases are often encountered with E/VAC copolymers having low vinyl acetate (VAC) content, where subheadings 3901.10 and 3901.30 may apply. In this instance, the precise determination of the comonomer content becomes critical.

E/VAC is widely used in industry, the applications depending on the VAC content. Examples include clear films for the packaging industry (2-5% VAC (m/m)), high performance films (7.5-12% VAC (m/m)), hot melt adhesives (21-40% VAC (m/m)), or cable engineering materials (<30% VAC (m/m)) [1].

In this work, Fourier Transform Infrared (FTIR) spectroscopy has been applied to determine percent VAC relative to the ethylene monomer unit (E) in E/VAC having a low VAC content. This technique is both fast and reliable and its usefulness has already been proven in the previous work [2-4]. A short study has been conducted to extend previous investigations by focusing on optimizing the band selection and performing statistical analysis to calculate the experimental precision error.

Commercial products, including DuPont's "Elvax", Bayer's "Baylon" and "Levapren", Dow's "Zetafax" and Quantum Chemical's "Petrothene" of known composition were used. These samples had

a stated nominal vinyl acetate content from 1.5 to 45% by weight.

## **EXPERIMENTAL**

### **1 PRINCIPLE**

The VAC content is determined by FTIR. The method consists of pressing thin films of E/VAC, recording FTIR spectra and calculating the ratio of selected optical densities (OD) corresponding to VAC and E bands. The optical densities are determined using peak heights or peak areas.

### **2 APPARATUS**

**2.1 Compression moulding press** with heated platens, capable of achieving a pressure of 4.5 MPa and a platens temperature of 170°C.

**2.2 FTIR spectrometer**, of wave number range 3700  $\text{cm}^{-1}$  to 400  $\text{cm}^{-1}$ .

#### NOTE:

In this study, FTIR spectra were obtained on a Perkin-Elmer 1600 spectrometer using ten scans with a resolution of 4.0  $\text{cm}^{-1}$ . Up to six different samples were measured for each nominal composition. Peak heights and peak areas were measured from a sloped baseline drawn through adjacent valleys using a GRAMS/386 software package.

### **2.3 Film holder**

## **3 PROCEDURE**

### **3.1 Preparation of films**

Mould the films using compression moulding press (2.1), lined with aluminum foil at a temperature of approximately 170°C and pressure adjusted to obtain a film thickness between 50  $\mu\text{m}$  to 100  $\mu\text{m}$  (approximately 4.5 MPa (650 psi)).

## NOTES:

1. To avoid possible thermal decomposition of the product, pressing time should be limited to 1 min.
2. To facilitate film release, (e.g. for low molecular weight E/VAC), extra layers of Kapton or Teflon [5] liner could be applied.

**3.2 Measurement**

- 3.2.1 Scan the background.
- 3.2.2 Record the spectrum using minimum of 10 scans.
- 3.2.3 Ratio the spectrum and convert into absorbance.
- 3.2.4 Select the best resolved peak among 610, 1020 or 3460  $\text{cm}^{-1}$  of the VAC bands (the complete band assignment is listed in Table 1), establish the baseline by drawing a straight line through adjacent valleys, and measure the optical density as the peak height, or for better results use peak areas (compare results in Figures 2, 3 and 4).
- 3.2.5 Repeat procedure 3.2.4 for E peak at 720  $\text{cm}^{-1}$ .
- 3.2.6 Determine the ratio of selected optical densities corresponding to VAC and E bands.

**4 EXPRESSION OF RESULTS****4.1 VAC content  $\leq$  25% (m/m)****4.1.2 Optical density determination using peak heights**

Establish the VAC content as a percentage by mass applying the ratio of optical densities determined in 3.2.6 using one of the following formulas:

$$\text{VAC\% (m/m)} = [380 \times \text{OD}(3460/720)^h - 1.1] \pm 5.2\% \text{ (m/m)}$$

$$\text{VAC\% (m/m)} = [11.8 \times \text{OD}(1020/720)^h + 1.6] \pm 3.2\% \text{ (m/m)}$$

$$\text{VAC\% (m/m)} = [58.2 \times \text{OD}(610/720)^h + 0.7] \pm 4.9\% \text{ (m/m)}$$

Where:

380, 11.8, and 58.2 represent the slope values on the corresponding calibration curves (Figure 2, 3, and 4) determined from the least squares method;

$\text{OD}(3460/720)^h$ ,  $\text{OD}(1020/720)^h$ , and  $\text{OD}(610/720)^h$  are the optical density ratios as determined in 4.2.6 using peak heights;

-1.1, 1.6, and 0.7 represent the intercept values on the corresponding calibration curves (Figure 2, 3, and 4) determined from the least squares method; and

$\pm 5.2\%$ ,  $\pm 3.2\%$ , and  $\pm 4.9\%$  (m/m) represent the precision error at 95% confidence level calculated from deviations of any given reading from the best linear fit (standard deviations are listed in Table 2).

#### 4.1.3 Optical density determination using peak areas

Establish the VAC content as a percentage by mass applying the ratio of optical densities determined in 3.2.6 using one of the following formulas:

$$\text{VAC\% (m/m)} = [192 \times \text{OD}(3460/720)^a + 0.3] \pm 3.1\% \text{ (m/m)}$$

$$\text{VAC\% (m/m)} = [6.9 \times \text{OD}(1020/720)^a + 1.5] \pm 2.8\% \text{ (m/m)}$$

$$\text{VAC\% (m/m)} = [90.0 \times \text{OD}(610/720)^a + 0.6] \pm 4.3\% \text{ (m/m)}$$

Where:

192, 6.9, and 90.0 represent the slope values on the corresponding calibration curves (Figure 2, 3, and 4) determined from the least squares method;

$\text{OD}(3460/720)^a$ ,  $\text{OD}(1020/720)^a$ , and  $\text{OD}(610/720)^a$  are the optical density ratios determined in 3.2.6 using peak areas;

0.3, 1.5, and 0.6 represent the intercept values on the corresponding calibration curves (Figure 2, 3, and 4) from the least squares method; and

$\pm 3.1\%$ ,  $\pm 2.8\%$ , and  $\pm 4.3\%$  (m/m) represent the precision error at 95% confidence level calculated from deviations of any given reading from the best linear fit (standard deviations are listed in Table 2).

#### 4.2 VAC content between 25 and 45% (m/m)

Establish VAC content as a percentage by mass using the ratio of optical densities determined in 3.2.6 (using either peak heights or peak areas) and reading VAC% (m/m) directly from the corresponding calibration curve (Figure 5, 6, or 7).

### RESULTS AND DISCUSSION

The representative, expanded reference spectra of E/VAC copolymers are shown in Figure 1 while all the relevant monomer bands are included in Table 1. The following suitability considerations have been made for the band selection:

- 3460  $\text{cm}^{-1}$  This isolated VAC band is suitable, however it may be obstructed by the presence of the interfering -OH or -NH absorptions (e.g. from antioxidant additives), particularly at low VAC levels. Therefore, the use of other VAC bands may become necessary.
- 2678  $\text{cm}^{-1}$  Although reported to have been used successfully as an E band [**3 and references therein**], this band appeared to be an impractical choice in our method due to its complexity (it is a shoulder on a much stronger CH absorption). In particular, it is very difficult to draw a correct baseline.
- 1743  $\text{cm}^{-1}$  This band is too intense. Generally, an OD should be less than 0.7 on the absorbance scale [**6**].
- 1465  $\text{cm}^{-1}$  This band is not suitable because it includes bending modes of both constituent monomer units.
- 1372  $\text{cm}^{-1}$  This band is not the best choice since it includes stretches of both  $\text{CH}_3$  groups from VAC and E (branching and terminal), and it can be further obstructed by additives.

- 1250  $\text{cm}^{-1}$  This VAC band is too intense.
- 1020  $\text{cm}^{-1}$  This is a fairly well resolved, medium intensity band of VAC.
- 720  $\text{cm}^{-1}$  The band of choice for E. This peak often appears as doublet due to crystal field splitting.
- 610  $\text{cm}^{-1}$  The band has a complex character, however baseline selection can be accomplished with ease.

The VAC% (m/m) data points obtained by this method are presented in the calibration curves as an average of three to six trials (Figures 2-7). For the low vinyl acetate range i.e., between 1.5-25% (m/m), where linearity was observed, a set of equations has been constructed. These equations describe straight lines shown in Figures 2-4. The slope and the intercept parameters in these equations have been obtained from the linear least-squares method. Figures 5-7 may serve as "manual" calibration curves for VAC determination outside the linear range.

For all the band ratios throughout this study, relatively good reproducibility parameters were obtained. Peak areas generally gave better precision in VAC determinations than peak heights which were consistently manifested in lower values of the calculated precision error. These values relate to linear approximation of the experimental results and were calculated at 95% confidence level using ordinates of the Normal Distribution Curve [7].

It was found that if VAC content is below 8% by weight, the use of the overtone band at  $3460 \text{ cm}^{-1}$  becomes impractical due to increasing interference from moisture and/or other hydroxylic species.

The best value of precision error of  $\pm 2.8\%$  VAC (m/m) obtained by this method (paragraph 4.1.3) indicates that the method can be routinely applied to "screen" E/VAC samples. Statistically, it means that for the given example, 95% of all the readings are expected to be accurate to within  $\pm 2.8\%$  VAC. The remaining 5% would reside outside these limits. When VAC content was back-calculated using linear equations described under Sections 4.1.2 and 4.1.3 and compared to the "original"



nominal content, the results (see Table 3) appeared well within limits of accuracy error. However, in borderline situations (practically, if VAC content is between 3 to 7% (m/m)), a more precise method should be used. The acidimetric titration which has been reported repeatable to between 0.3-0.5% (m/m) seems to be good alternative, but its precision error remains to be determined [2].

### CONCLUSION

For the FTIR analysis of E/VAC, it was found that the most precise results were obtained by determining the optical density ratio at  $1020\text{ cm}^{-1}/720\text{ cm}^{-1}$  and by using the technique of peak integration. The method's precision was limited to  $\pm 2.8\%$  VAC.

### ACKNOWLEDGEMENT

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Special thanks are directed to Mr. Ronald E. Roller, Research Specialist at Quantum Chemical, USI Division in Cincinnati, Ohio for providing valuable E/VAC standards with low VAC content.

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7. Chemical Engineers' Handbook, Perry and Chilton, McGraw Hill, 5th Ed., 1973, Table 1-19, page 1-38.

## Table 1

**Comonomer Contributions and IR Band Assignments of  
E/VAC Copolymers**

ethylene	vinyl acetate	band interpretation
$\text{cm}^{-1}$		
	3460	overtone of C=O at 1743 $\text{cm}^{-1}$
2678		CH <sub>2</sub> stretching
	1743	C=O stretching
1465		CH <sub>2</sub> bending
	1372	CH <sub>3</sub> bending
	1250	C-O stretching of (C=O)-O
	1020	C-O stretching of O-CH
720		(CH <sub>2</sub> ) <sub>n</sub> n≥4 rocking
	610	CH <sub>3</sub> -(C=O)-O bending

**Table 2****Standard Deviations of the Optical Density Ratios\***

Optical Density Ratio	Standard Deviation	
	height	area
3640 $\text{cm}^{-1}$ /720 $\text{cm}^{-1}$	0.00692	0.00815
1020 $\text{cm}^{-1}$ /720 $\text{cm}^{-1}$	0.140	0.205
610 $\text{cm}^{-1}$ /720 $\text{cm}^{-1}$	0.0432	0.0246

\*based on deviation of any given reading from the least-squares line

### Table 3

#### Determination of Vinyl Acetate Content in E/VAC Copolymer

nominal <sup>a</sup>	Vinyl Acetate Weight Percent					
			calculated <sup>b</sup>			
	3460/720		1020/720		605/720	
1.5	ND <sup>c</sup>		2.0	(2.5)	2.1	(2.2)
2.5	ND		2.6	(3.3)	3.0	(2.7)
4.5	ND		3.1	(4.0)	4.7	(4.3)
8	7.4	(6.9)	8.5	(8.0)	7.1	(7.1)
9	9.1	(9.8)	9.7	(9.1)	9.3	(9.9)
12	12.6	(12.4)	10.1	(9.6)	11.1	(11.1)
15	15.3	(14.6)	15.7	(14.7)	13.6	(13.5)
18	18.0	(18.8)	18.3	(17.8)	18.3	(18.7)
25	24.9	(25.6)	24.9	(26.6)	26.2	(25.7)

<sup>a</sup>as claimed by the manufacturer

<sup>b</sup>calculated for the indicated optical density ratios using peak areas and linear equations from paragraph 4.1 (numbers in parentheses represent results obtained using corresponding peak heights)

<sup>c</sup>result not determined

Figure 1

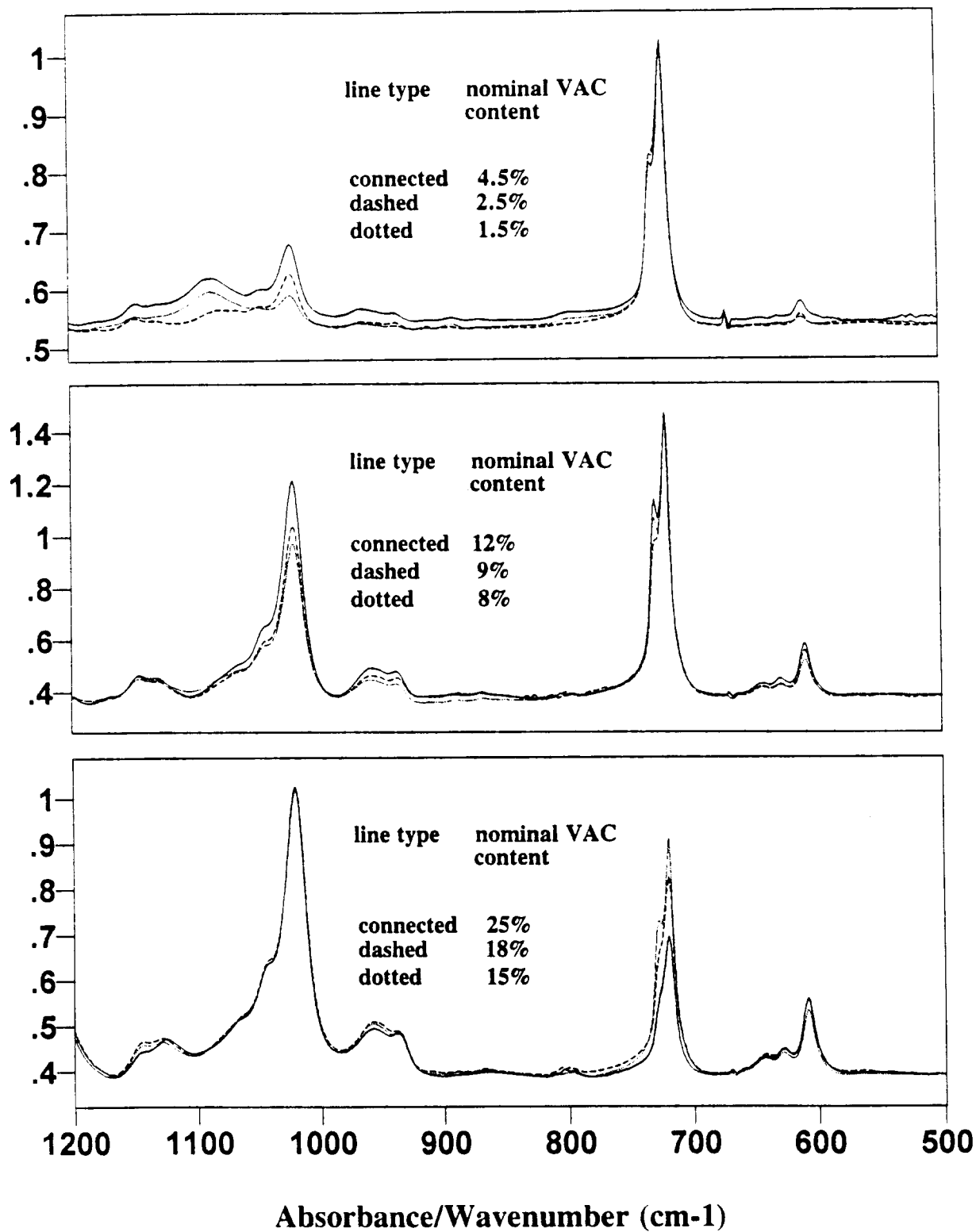


Figure 2

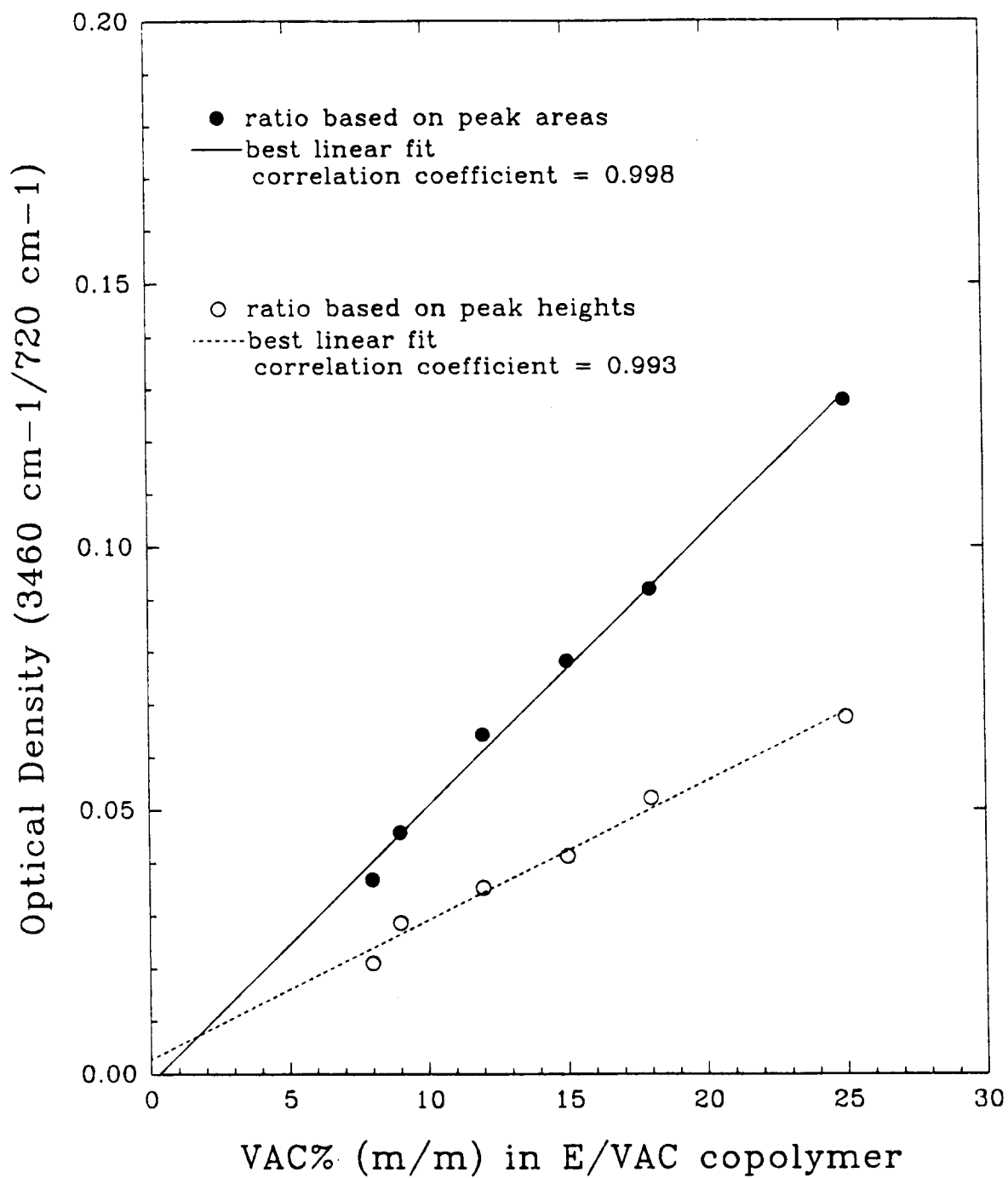


Figure 3

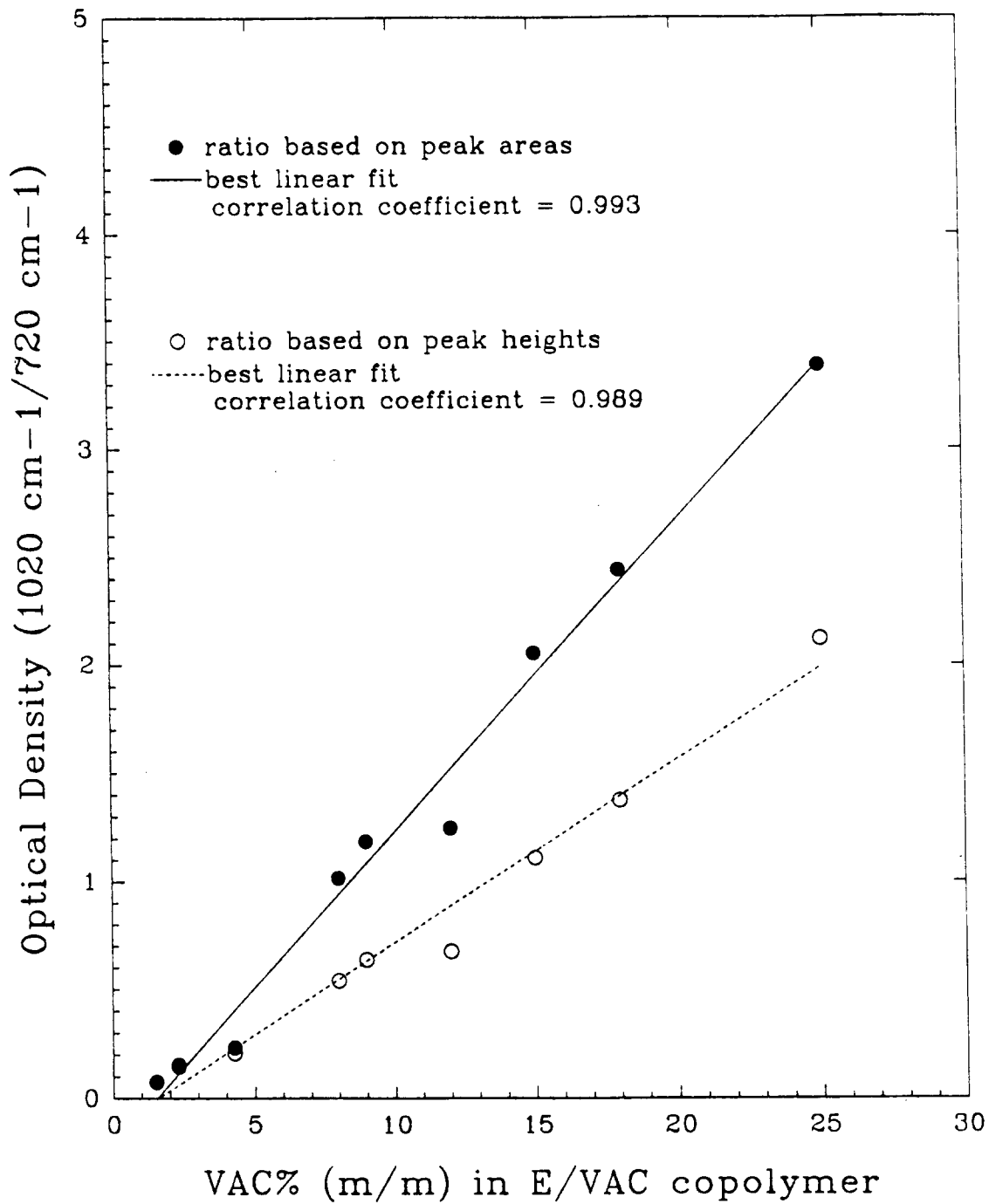




Figure 4

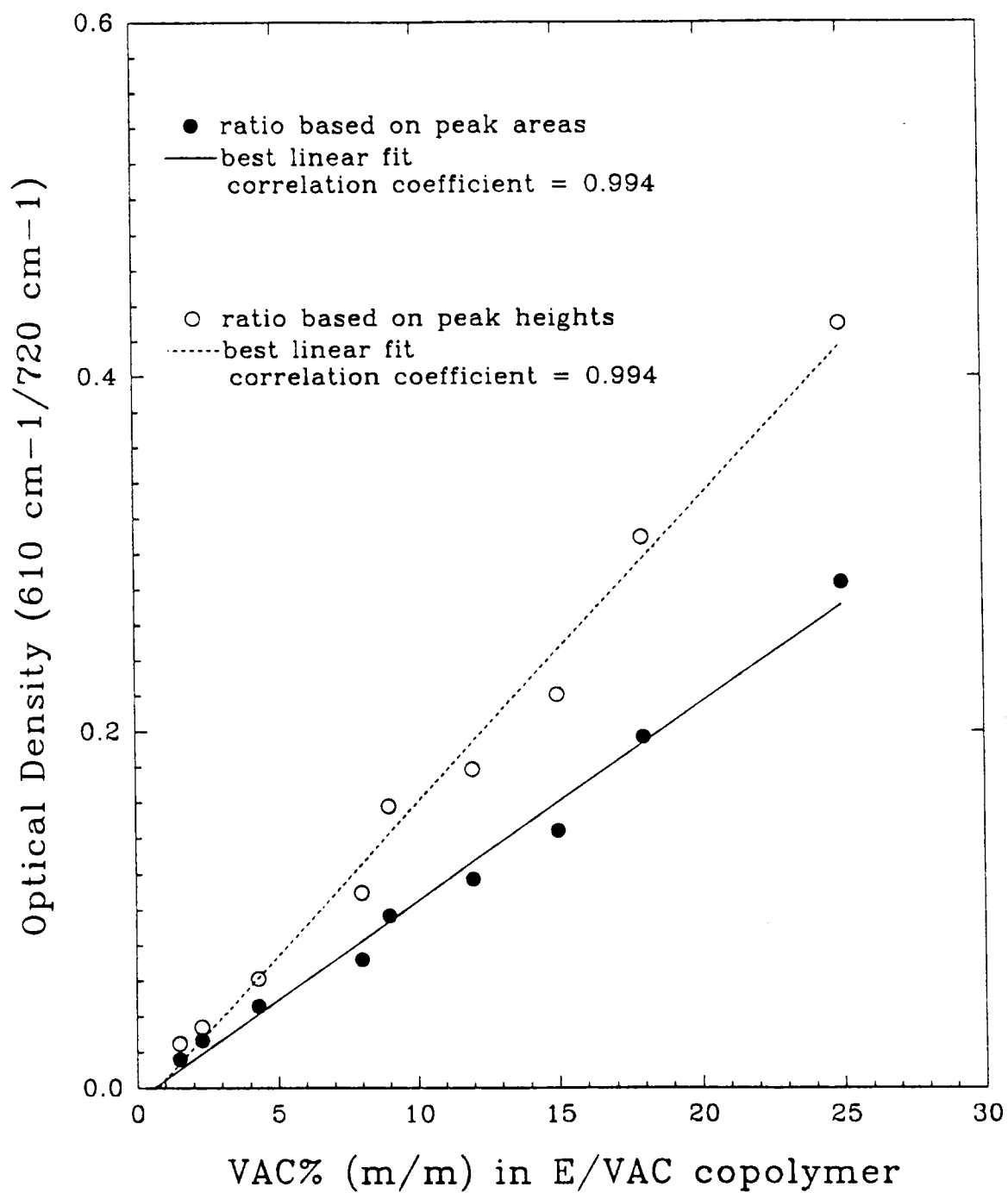
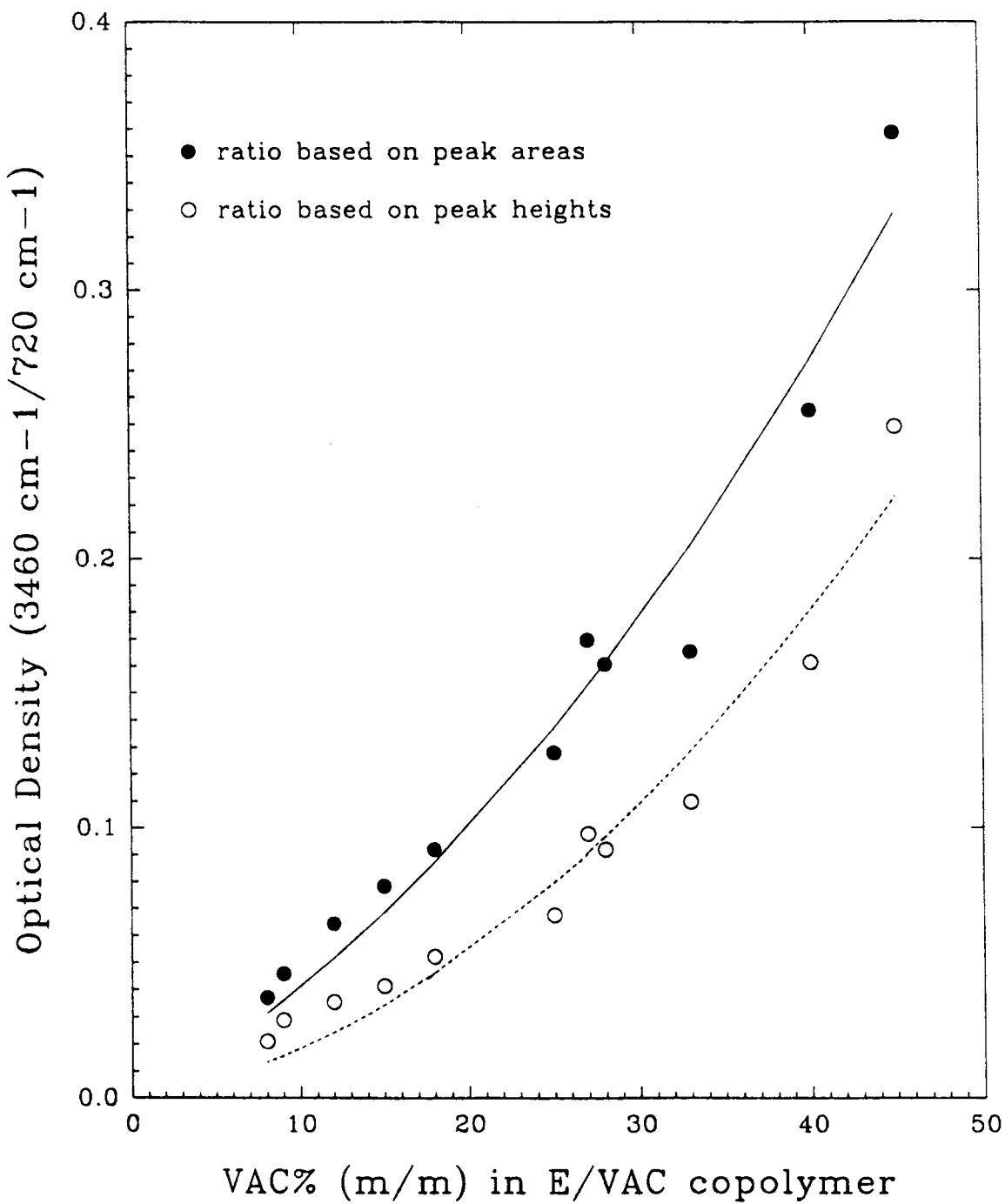
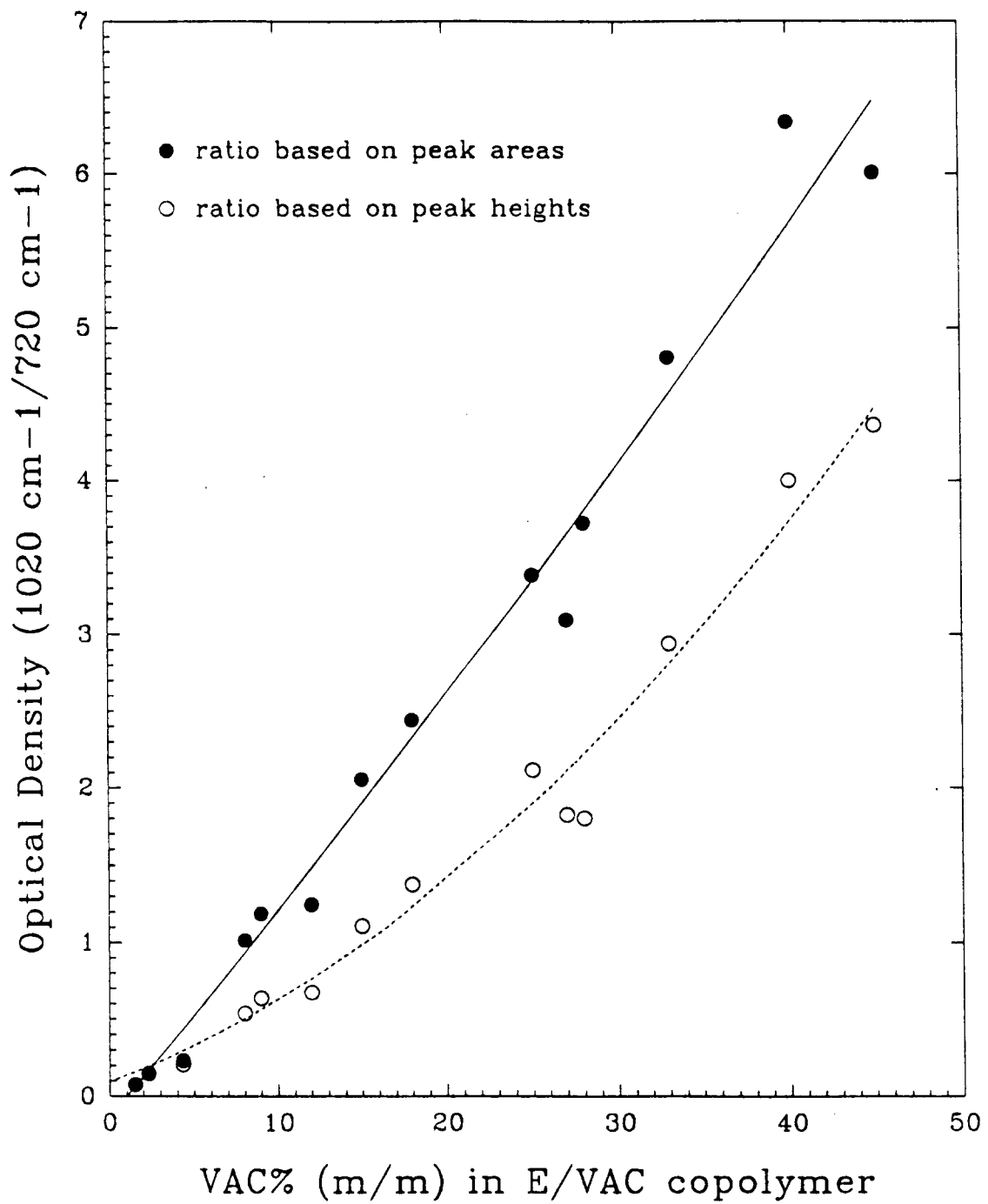


Figure 5



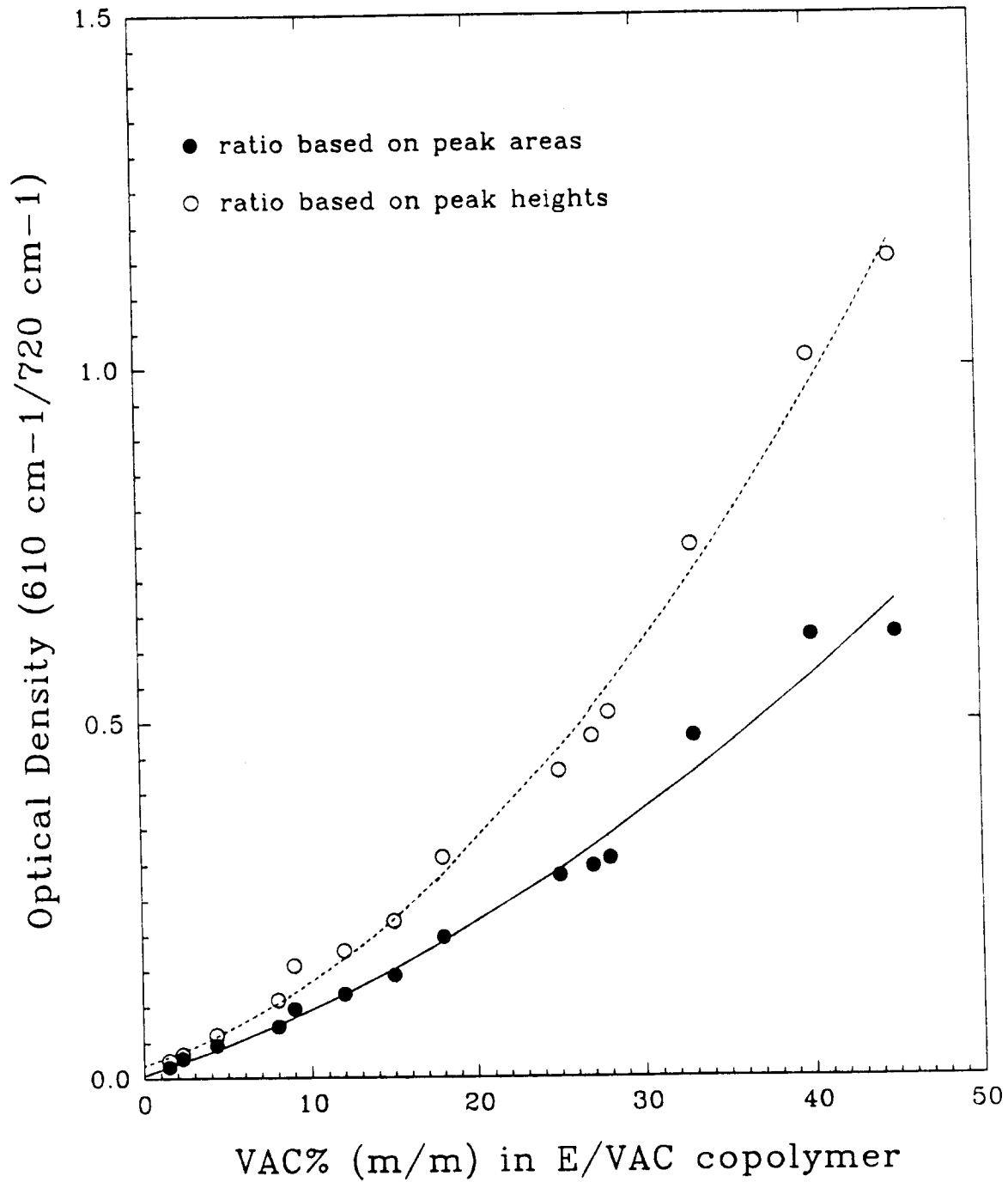
points connected for clarity

Figure 6



points connected for clarity

Figure 7



points connected for clarity

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**THE MEASUREMENT OF SOFT SPRINGBACK AND IMPACT  
ABSORPTION PROPERTIES OF ERGONOMIC POLYURETHANE  
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**INTRODUCTION**

The Canadian government had been requested by industry to provide special tariff treatment for ergonomic grades of polyurethane (PU) foams which are commonly used for comfort cushioning in wheelchairs and other medical devices. The following tests were developed to provide simple and efficient methods to differentiate this type of foam from other PU foams.

The unique compression-deflection behaviour of ergonomic foams results not only from their chemical composition, but most importantly from their open cell structure that allows the free movement of air inside the foam when it is deflected [1]. The resulting properties include low rebound, good energy absorption (typically in excess of 90%) and gradual but complete recovery from intermittent loadings.

Standard methods for testing of moulded urethane foams are compiled under comprehensive ASTM method D 3574 [2]. Indentation load deflection (ILD) Tests B<sub>1</sub> and B<sub>2</sub> are often used to measure cushioning capabilities, while "Ball Rebound" Test H is used for testing resilience or energy absorption properties. None of the standard tests however measures simple dynamic properties such as the rate of recovery from deflection. For example, Test D of the above mentioned ASTM method (a "Constant Deflection Compression Set Test") only measures the degree of recovery, but not the speed of recovery.

In the present work, a new test has been developed to measure the recovery time of deflected foams and a "Ball Rebound" Test H of ASTM D 3574 has been adopted with some modifications.

## EXPERIMENTAL

### Test 1

#### CONSTANT DEFLECTION TEST - SPECIFIED SET (Supplemental Method for ASTM D 3574) [2]

##### 1. Summary of Method

The method measures the time necessary for the deflected foam specimen to recover from 25% to 75% of its original thickness.

##### 2. Apparatus

- *Compression Device*, consists of a flat plate equipped with a handle which is used on a flat surface, e.g., laboratory table;
- the required deflection is achieved by the use of *spacers*;
- the time of recovery is measured using a *stopwatch* having a LCD display and an accuracy of 1/100 of a second;
- the 75% set is established using a ruler with the smallest division of 1 millimetre; and
- the recovery time is determined using a *videocamera* to record the recovery and a suitable *viewing system* enabling the play back of the recovery process in slow motion.

##### 3. Test Specimens

The test specimens must have parallel top and bottom surfaces and minimum dimensions of 50 mm by 50 mm and 38 to 51 mm thick.

##### 4. Procedure

- the entire test procedure is conducted at  $23 \pm 2^\circ\text{C}$  and

50 ± 2% relative humidity and is continuously monitored and recorded by the use of videocamera;

- the specimen is deflected and held at 25% of its original thickness for approximately 1 minute;
- the compression plate is removed quickly;
- the time ( $t_0$ ) at which the compression plate is removed and the time ( $t_{75}$ ) at which the flat top of the specimen reaches 75% of its original height are determined during the play-back of the recovery process. Some samples will deform during recovery. This situation may occur when the foam has very small cells. In this instance the thickness of the specimen at its centre should be monitored.
- if the recovery time measurements are repeated on the same specimen, a minimum interval time of 5 minutes should be allowed between each trial.

## 5. Calculations

The recovery time  $t_r$  necessary for the deflected specimen to recover from 25% to 75% of its original thickness is calculated, as follows:

$$t_r = t_{75} - t_0$$

where:

$t_r$  indicates recovery time expressed in seconds;

$t_{75}$  indicates time at which recovery reaches 75% of original height; and

$t_0$  indicates time at which recovery begins.

Calculate the mean of at least three trials. If any value deviates more than 20% from this mean, make two additional trials and calculate the mean for all five trials.

## 6. Report

Report the calculated recovery time in seconds.

### Test 2

#### **RESILIENCE (BALL REBOUND) TEST (Modified ASTM D 3574 Test H)[2]**

##### 1. Summary of Method

The test consists of dropping a steel ball on a foam specimen and noting the height of the rebound (bounce).

##### 2. Apparatus

- a *ball rebound tester* consists of a clear, vertical plastic tube, such as acrylic, with 38 mm inside diameter;
- a *steel ball* of a diameter of 16 mm and a weight of 16.3 g is released into the plastic tube without rotation. The height of the drop is 500 mm above the specimen surface (the top of the ball is positioned 516 mm above the surface of the foam. "Zero" rebound is equal to the diameter of the ball);
- a *ruler* with the smallest division of 1 mm is positioned beside the tube; and
- a *videocamera* and *viewing system* enabling play back in slow motion is used to allow good precision in determining the amount of rebound.

##### 3. Test Specimens

The test specimens must have parallel top and bottom surfaces and minimum dimensions of 50 mm by 50 mm and at least 38 mm thick.

##### 4. Procedure

- the entire test procedure is conducted at  $23 \pm 2^\circ\text{C}$  and  $50 \pm 2\%$  relative humidity and is continuously monitored and recorded by the use of videocamera;



- the specimen is positioned at the base of the tube. The tube and the ruler are adjusted so that "zero rebound" is 16 mm above the surface of the foam specimen;
- the ball is released from the centre top of the tube;
- the height of the rebound is determined during the play-back of the rebound process. If the ball strikes the tube on the drop or rebound, the value obtained is invalid.

## 5. Calculations

The rebound is expressed as a percentage of the release height, as follows:

$$\text{Rebound (\%)} = (h_b / 500 \text{ mm}) \times 100$$

where:

$h_b$  indicates height of rebound (bounce) expressed in millimetres; and

500 mm indicates the height of ball drop

Calculate the mean of at least three rebound values. If any value deviates more than 20% from this mean, make two additional drops and calculate the mean for all five drops.

## 6. Report

Report the calculated Ball Rebound Resilience Value of the sample as a percentage.

## RESULTS AND DISCUSSION

The average recovery times and the average rebounds were measured using Test 1 and Test 2, respectively. The temperature of  $23 \pm 2^\circ\text{C}$  and the relative humidity of  $50 \pm 2\%$  were selected for both tests to meet conditions reported in the ASTM method D 3574 [2]. Various grades of PU foams have been tested and the results are included in Table 1. Samples with designations A

through E and F through H, respectively, represent two different sets of ergonomic PU foams obtained from two independent manufacturing sources. An "ordinary" polyurethane household sponge (sample I), with an open cell structure has also been tested for comparison.

Within the first series (samples A through E), the ball rebound values were found to decrease from approximately 14% to approximately 8% as the recovery times increased from 1.1 second to 2.6 seconds. The rebound was also found to be inversely proportional to the sample's firmness within this series. Although the values of relative firmness were unknown for the second set (samples F through H), a similar rebound/recovery pattern was observed. Generally, the higher the ball rebound, the shorter the time for the sample to recover from deflection. Recovery times fell within a relatively narrow range for all tested specimens of ergonomic foams, essentially, within 0.5 - 3.0 seconds. The rebound, on the other hand showed a greater diversity. For example, sample H exhibited remarkable dampening properties with a barely measurable rebound at 0.2%, while in case of sample A, the ball rebounded to a sizable 14%.

The "ordinary" polyurethane household sponge behaved quite differently. Not only did it have a clearly distinguishable ball rebound of 26%, but its recovery time from deflection was more than an order of a magnitude shorter than any tested ergonomic foam.

## **CONCLUSION**

The soft springback property of ergonomic polyurethane foam was effectively expressed in terms of recovery time necessary for the deflected foam specimen to recover from 25% to 75% of its original thickness. The high impact absorption, another unique property of ergonomic PU foam, was determined using a modified ASTM ball rebound test [2]. For both properties, video equipment with slow motion playback capabilities was necessary to make the measurements. The soft springback and the high impact absorption properties were useful in distinguishing between ergonomic grades of PU foams and other PU foams.

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**REFERENCES**

1. Meinecke, E.A. and Clark, R.C., "Mechanic Properties of Polymeric Foams", Technomic, 1973
2. Standard Methods of Testing for Flexible Cellular Materials - Slab, Bonded, and Moulded Urethane Foams, ASTM D 3574-77, p. 471.

**Table 1**

**Experimental Results for Average Recovery Time in  
Test 1 and Average Rebound in Test 2**

<u>Sample<sup>a</sup></u>	<u>Recovery time</u>	<u>Rebound</u>
	[s]	[%]
<b>A</b> soft (0.73 PSI)	1.28	14.5
<b>B</b> medium-soft (0.82 PSI)	1.10	10.4
<b>C<sup>b</sup></b> medium (0.92 PSI)	1.3	8.9
<b>D</b> medium-firm (0.99 PSI)	1.60	7.0
<b>E</b> firm (1.20 PSI)	2.63	8.5
<b>F<sup>c</sup></b>	0.65	0.93
<b>G<sup>c</sup></b>	1.08	0.40
<b>H<sup>c</sup></b>	1.13	0.20
<b>I<sup>b,d</sup></b>	0.05	26.0

a numbers in parentheses indicate support pressure in pounds per square inch (relate to the firmness of the foam) as claimed by the manufacturer

b 38 mm thick specimen

c ergonomic foam of undisclosed firmness and support pressure

d an open cell polyurethane household sponge

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