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Use of an Oligomer as an Internal Standard in Gel Permeation Chromatography

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Synopsis

The application of an oligomer as an internal standard in gel permeation chromatography was studied on narrow low molecular weight fractions of linear polyethylene using *n*-decane as the standard. A Waters gel permeation chromatograph was run continuously at 130°C with *o*-dichlorobenzene as solvent. It has been found that the values of the elution volume of given samples vary with time and that a simple correction using *n*-decane as an internal standard reduces the inaccuracy from the original 6% to less than 1%. The corrected elution volumes remain reproducible over a period of several months so that frequent calibration is eliminated. The use of the oligomer chemically similar to the polymer samples gives a much better result than the use of low molecular weight impurity as the standard.

INTRODUCTION

Gel permeation chromatography (GPC) is a rapid and useful method of measuring molecular weight and molecular weight distribution of polymers using a calibration curve prepared under identical experimental conditions. However, the elution volume will be affected by experimental conditions like the temperature of the oven and the siphon and the flow rate,[1,2] all of which may vary under the usual operational conditions of the instrument due to factors like change of ambient temperature, blocking of filters, and deterioration of columns. Reliance on a preexisting calibration will therefore introduce inaccuracies. In our experience, such inaccuracies in molecular weight could amount to more than 5%. High accuracy and a good reproducibility was very essential in the measurements of chain lengths of polyethylene degraded by nitric acid and ozone.[3] For this reason, we introduced an internal standard in our experimentation by which experimental errors of the kind just listed can be eliminated. Here, we shall report on our experience with internal standards and on the most desirable method established.

To be meaningful, the internal standard in GPC should have the chemical composition identical to the specimens and elute several pulses (about 10 to 15 ml) after the elution of the lowest molecular weight fraction of in-

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terest. Any deviation in the elution volume of the specimen due to the change of temperatures of the oven and the siphon, the flow rate, and the column efficiency can be easily found out from the elution volume of the internal standard. The ratio of the elution volume of the internal standard in a given run to that for the same internal standard in a calibration run can be used as a coefficient for correcting the elution volume of an unknown sample back to the calibration conditions,[4] i.e.,

$$V_{corr} = V_{ob} \frac{S_{cal}}{S_{ob}}$$

where V_{corr} = the corrected sample elution volume, V_{ob} = observed sample elution volume in a given run, S_{cal} = internal standard elution volume used for preparing of the calibration curve, and S_{ob} = observed internal standard elution volume in a given run.

A different approach was chosen by Williams et al.,[5] who used internal standards chemically different from the specimen with the values of elution volume covering the whole range of specimen elution volume. The specimen and the standards were eluted simultaneously and the superimposed spectra were resolved by two different detectors. The advantage of the method is that the calibration points are distributed over the range of elution volume of interest, the disadvantage is that two detectors are necessary. Also, it is possible that the dependence of the elution volume on the experimental conditions can be different for the specimen and standards if the chemical composition of the specimen and standards is not the same.

EXPERIMENTAL

A Waters gel permeation chromatograph was used with a series arrangement of four columns. The columns used for calibrations 22 and 23 had 1.5×10^5–5×10^4, 1.0×10^4, 850, and 300 Å permeability limits; and those used for calibrations 26 and 29 had 1.5×10^5–5×10^4, 1.0×10^4, 2000–700, and 350–100 Å permeability limits. Distilled *o*-dichlorobenzene was used as a solvent, with a column temperature of 130°C. The flow rate was 0.8 ml/min. The injected weight of polymer in solution was 4 mg, and full volume of the sample loop (2 ml) of solution was injected.

There was no deliberate addition of an interval standard for calibrations 22 and 23, while *n*-decane was introduced for calibrations 26 and 29. *n*-decane 0.03% w/v solution in distilled *o*-dichlorobenzene was used as a solvent for calibration samples of calibrations 26 and 29. All calibration samples were injected within two or three days. The time intervals elapsed between calibrations 22 and 23 and between calibrations 26 and 29 were the same and were of about five months each.

RESULTS AND DISCUSSION

All through the previous work in this laboratory, a peak of unspecified origin appeared at about 200 ml. We shall refer to this as "impurity peak"

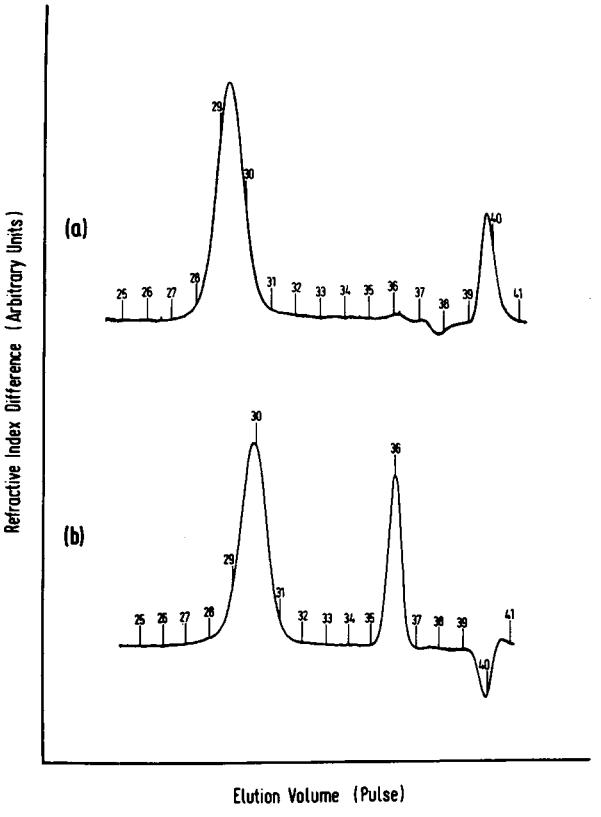

Fig. 1. GPC spectrum of sample PE183 without (a) and with (b) addition of *n*-decane.

shown, for example, in Figure 1a at 198.7 ml. In the absence of other standards we took this impurity peak as an internal standard. We shall compare the standardization achieved in this way with the result of subsequent experiments where an internal standard *n*-decane was deliberately added (peak at 180.2 ml in Fig. 1b).

Table I shows the observed elution volumes for the "impurity peak" and the observed and the corrected elution volumes for eight polyethylene fractions for calibrations 22 and 23. It can be seen that the observed elution volumes for the fractions and the impurity peak are lower for calibration 23 than for calibration 22, while the reverse is the case for the corrected elution volumes of the fractions. This introduces an uncertainty in the calibration.

The observed elution volumes for the fractions and *n*-decane and the corresponding corrected elution volumes for the fractions for the calibrations 26 and 29 are shown in Table II. Observed elution volumes for both the fractions and *n*-decane are lower for calibration 29 than for calibration 26; but after the correction has been made, the corrected elution volumes of the fractions are almost the same for both calibrations.

TABLE I
Comparison of Observed and Corrected Elution Volumes of Polyethylene Fractions Determined at Different Times Using Impurity as the Internal Standard[a]

Sample	log mol wt	Observed sample elution volume, ml		Observed impurity elution volume, ml		Corrected sample elution volume, ml	
		Cal 22	Cal 23	Cal 22	Cal 23	Cal 22	Cal 23
PE107	3.04	153.31	152.72	201.01	199.80	152.54	152.87
PE126	3.14	150.80	150.00	201.01	198.98	150.04	150.77
PE152	3.22	149.08	148.33	201.48	198.92	147.98	149.14
PE183	3.28	147.32	146.88	201.20	198.71	146.44	147.83
PE218	3.39	144.85	144.19	201.03	198.83	144.11	145.04
PE334	3.54	141.48	140.84	201.13	199.30	140.68	141.33
PE362	3.60	140.38	140.00	201.14	199.42	139.58	140.41

[a] Calibrations 22 and 23. Column set: 1.5×10^5–5×10^4 Å, 1.0×10^4 Å, 850 Å, and 300 Å. Standard impurity peak: 200 ml.

TABLE II
Comparison of Observed and Corrected Elution Volumes of Polyethylene Fractions Determined at Different Times Using *n*-Decane as Internal Standard[a]

Sample	log mol wt	Observed sample elution volume, ml		Observed decane elution volume, ml		Corrected sample elution volume, ml	
		Cal 26	Cal 29	Cal 26	Cal 29	Cal 26	Cal 29
PE107	3.04	154.32	154.28	179.77	179.35	154.52	154.84
PE126	3.14	152.44	152.17	180.00	179.43	152.44	152.65
PE152	3.22	—	150.33	—	179.34	—	150.88
PE183	3.28	149.64	—	180.18	—	149.49	—
PE218	3.39	146.36	145.54	180.00	178.82	146.36	146.50
PE246	3.44	145.73	144.34	180.84	179.00	145.05	145.15
PE334	3.54	142.77	142.48	180.00	179.32	142.77	143.02
PE362	3.60	141.95	141.63	180.00	179.60	141.96	141.94

[a] Calibrations 26 and 29. Column set: 1.5×10^5–5×10^4 Å, 1.0×10^4 Å, 2000–700Å, and 350–100 Å. Standard decane peak: 180.0 ml.

TABLE III
Reproducibility of Observed and Corrected Elution Volume of Polyethylene Fraction Determined Over a 5-Month Period of Continuous GPC Running[a]

Calibration no.	Calibration date	Observed sample elution volume, ml	Observed decane elution volume, ml	Corrected sample elution volume, ml
26	12/14/72	145.73	180.84	145.05
27	1/7/72	145.51	180.72	144.93
28	3/9/72	144.28	179.25	144.88
29	5/1/72	144.34	179.00	145.15
Mean value		144.96		145.00
Mean deviation		0.65		0.10

[a] Sample PE 246. Column set and standard decane peak are the same as in Table II.

Table III shows the observed elution volumes of *n*-decane and polyethylene fraction (PE 246) together with the corrected elution volumes of the fraction for four different calibrations. The mean value of these four observed and the mean value of the corresponding corrected elution volumes is the same (145.0 ml), but the mean deviation of the observed volumes is as high as 0.65 ml, whereas the deviation of the corrected data is only 0.10 ml. The molecular weight uncertainty has been thus reduced from about $\pm 6\%$ to better than $\pm 1\%$. An oligomer is more desirable as an internal standard than the impurity because of the following reasons:

The chemical composition of the oligomer is identical to that of the polymer (with the possible exception of the endgroups).

An oligomer elutes closer to the polymer than the impurity and the experimental errors are minimized.

In contrast to the impurity, the concentration of the oligomer can be controlled.

CONCLUSIONS

The use of an oligomer as an internal standard reduces considerably the uncertainty of the molecular weight measurement.

The variation of the calibration curve is eliminated and frequent calibration is avoided.

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