NISTIR 6054

Recertification of the SRM 1482a, a Polyethylene

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Final Report prepared for
Standard Reference Materials Program

U.S. DEPARTMENT OF COMMERCE
William M. Daley, Secretary

TECHNOLOGY ADMINISTRATION
Gary R. Bachula, Acting Under Secretary for Technology

NATIONAL INSTITUTE OF STANDARDS
AND TECHNOLOGY
Raymond G. Kammer, Director

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Gaithersburg, MD 20899

Certain commercial materials and equipment are identified in this paper to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply necessarily the best available for the purpose.

A final report prepared for the sponsors, Standard Reference Materials Program

Abstract

The recertification of a narrow molecular weight distribution poly(ethylene) Standard Reference Material, SRM 1482a, is described. Studies by size exclusion chromatography to obtain the bottle-to-bottle homogeneity are described. This method is also used to compare SRM 1482a with the material sold previously as SRM 1482. The intrinsic viscosity of SRM 1482a in 1,2,4-trichlorobenzene was determined to be 40.2 mL/g with a sample standard deviation of 0.54 mL/g, based on 6 degrees of freedom. A combined expanded uncertainty of 0.57 mL/g is estimated for this determination. The intrinsic viscosity measured for SRM 1482a is in excellent agreement with the intrinsic viscosity of 40.1 mL/g obtained for SRM 1482 by Wagner and Verdier in 1978.

1.0 Introduction

This report describes homogeneity testing and the recertification for intrinsic viscosity of a poly(ethylene), SRM 1482a. This material was originally certified in 1978 as SRM 1482 and is described in detail in the report describing that work [1]. Some of the original material was rebottled by the Standard Reference Materials Program (SRMP) into smaller samples to conserve the remaining stock. On the event of the rebottling of the material, the intrinsic viscosity of the polymer was measured again and compared with the earlier measurements. A bottle-to-bottle variability study on the rebottled material, SRM 1482a, was also made by size exclusion chromatography (SEC).

2.0 Preparation, Bottling, and Sampling of SRM 1482a

2.1 Preparation

The preparation and purity determinations on SRM 1482a are described in a report on SRM 1482 [1]. The molecular weight standard is in the form of a powder.

2.2 Bottling and Sampling of SRM 1482a

A total of 208 samples, about 0.4 g each, were bottled in amber vials. The entire set of samples was divided into six subsets. One vial was randomly selected from each subset for homogeneity testing. In the following, the containers holding SRM 1482a and SRM 1482 will be referred to as vials. Two vials of the original bottling made 20 years ago of SRM 1482 were obtained from SRMP. These were used in the subsequent studies to determine whether the rebottled material differed from the originally bottled material.

3.0 Homogeneity Testing on SRM 1482a and SRM 1482

3.1 SEC on SRM 1482a and SRM 1482

This testing was accomplished using SEC. In this study, a Waters 150-C AL/GPC Liquid Chromatograph (Waters Corp., Milford, MA) with a differential refractive index (DRI) detector and a single Jordi 50 cm X 10 mm ID Linear Mixed Bed GPC (Jordi Associates, Billingham, MA) column was used. The chromatograms were taken at 0.8 mL/min solvent flow rate. The injector and column compartments of the Waters 150-C AL/GPC were controlled at 130 °C for all measurements. The solvent, 1,2,4-trichlorobenzene (TCB), was obtained from Aldrich Chemical (1,2,4-trichlorobenzene, 99+ %, spectrophotometric grade, Aldrich Chemical, Milwaukee, WI) and used as received. Santonox (5-tert-Butyl-4-hydroxy-2-methylphenyl sulfide), also obtained from Aldrich Chemical, was added to the solvent at about 0.1 g/L as an antioxidant.

Vials of SRM 1482 and SRM 1482a were obtained from SRMP as described above. An additional supply of the polymer, used for later experiments including the intrinsic viscosity measurements reported herein, was taken from a supply of SRM 1482 stored in the NIST Polymers Division. This material will be referred to as the division supply.

2 mg to 4 mg of the polyethylene samples were weighed into the canister of the Waters auto filtration assembly along with 4 mL of solvent yielding a concentration of approximately 1.0 g/L. Hexadecane at 0.03 mL/L was added to the solutions of polymer and solvent as a marker to indicate the reproducibility of the solvent volume delivered by the SEC pump for all measurements. Each filtering assembly was heated to 150 °C in an oven for about 1.5 h and the solution was shaken at frequent intervals to aid the dissolution. The filter assemblies were placed in the Waters 150-C AL/GPC injection compartment held at 130 °C for automatic filtering and injection. Chromatograms were then run with these solutions.

Solutions were prepared from each vial of SRM 1482, of SRM 1482a, and from the division supply. Two solutions were prepared from each vial received from SRMP and four solutions were prepared from the division supply. The order used to run the solutions was randomized following the method described in section 1-4 of Natrella [2]. Two injections were made from each solution.

After baseline subtraction, the SEC chromatograms were normalized to unit peak height and compared initially by overlaying to determine if there were visible differences outside the noise. The chromatograms from different solutions all superimpose on each other. This preliminary comparison showed that polymer samples taken from all the vials produced identical chromatograms. Further statistical analysis of the chromatograms is discussed in section 3.2.

3.2 Statistical Method to Compare Chromatograms

3.2.1 Match Factor

In earlier SRM SEC studies the match factor was used to compare one chromatogram to all the others. This factor is a correlation coefficient between one chromatogram and another. The match factor is defined by Huber [3] as

$$\text{Match Factor} = 10^3 \{\sum x^*y - (\sum x^* \sum y)/p\}^2 / [\{\sum x^2 - \sum x^* \sum x/p\}\{\sum y^2 - \sum y^* \sum y/p\}]. \quad (1)$$

The values x and y are the measured signal in the first and second chromatograms respectively at the same time in the chromatograms; p is the number of data points. The sums are taken over all data points.

At the extremes, a match factor of zero indicates no match and 1000 indicates an identical chromatogram. Generally, values above 990 indicate that the chromatograms are similar. Values between 900 and 990 indicate there is some similarity, but the result should be interpreted with care. All values below 900 are thought to mean that the chromatograms are different [3,4] .

Fig. 1 gives the match factor against the first chromatogram for the entire set of chromatograms which include two injections for each solution prepared.

An ANOVA study using OMNITAB [5] made on the match factors obtained from the chromatograms indicated that the match factors for the chromatograms from the same vial were no different than those from different vials on a level of significance with $\alpha = 0.05$ [2]. Moreover, the match factors of chromatograms from bottles of SRM 1482 and bottles of SRM 1482a were indistinguishable using the same significance level with $\alpha = 0.05$. The samples were run in groups of 6 to 8 on different days. Using the match factor we did find one day was slightly different from the rest on a level of significance with $\alpha = 0.05$.

As described above, hexadecane was added to the solutions of polymer and solvent, as a marker to indicate the reproducibility of the solvent delivered by the SEC pump for all the above measurements. These hexadecane peaks were widely separated from the peaks for the polyethylene, and thus were separately analyzed in a match factor method similar to that described above for the polyethylene chromatograms. Any variation in these would indicate chromatographic system variations and not sample-to-sample variations. Thus, an ANOVA study using OMNITAB made on the match factors obtained from the hexadecane chromatograms indicated that the match factors for the chromatograms from the same vial were no different from those from different vials on a level of significance with $\alpha = 0.05$ [2]. Moreover, the match factors of hexadecane chromatograms associated with bottles of SRM 1482 and bottles of SRM 1482a were indistinguishable on a level of significance with $\alpha = 0.05$. Using the match factor, we did find that the match factor for any day was different from that of any other day again at the level of significance with $\alpha = 0.05$.

3.2.2 Principal Component Analysis of Chromatograms

To make a more comprehensive study of the chromatograms, we have developed a method to compare chromatograms using a Principal Component Analysis (PCA). We follow the notation and conceptualization of Johnson and Wichern [6] in what follows. Each chromatogram is divided into areas of equal time width. The time width, about 5 s, is selected to be small enough to show fine structure such as a shoulder on the chromatogram. Each area over this time interval was then taken to be a_{ij} where the index j, the matrix column index, is on the jth measurement, in this case the jth chromatogram. The index i refers to the ith time interval or the ith elution volume. The

matrix of the a_{ij}, A, is a p by n matrix where the number of volume elution intervals in each chromatogram is p and the number of chromatograms measured is n. Thus, each chromatogram is represented by a column vector of the matrix A whose ith element is the area of the chromatogram in the time interval i.

For our further analysis, we will study the PCA of $D = A A^T$. Thus $d_{ij} = \sum_k a_{ik} a_{kj}^T$ where the sum is over the chromatograms.

The D matrix is diagonalized and the eigenvalues and their associated eigenvectors obtained. In table 1 we show the first four eigenvalues and the percent of the contribution to the total sum of eigenvalues (the trace of the D matrix) they give. Notice the first eigenvalue accounts for 99.5 % of the sum of the eigenvalues and the first two together account for all but 0.04 % of the sum of eigenvalues. This indicates that the first and second vectors completely describe our system. Figure 2 shows the first and second principal vectors of the D matrix. Scores (the dot product of any specific chromatogram with the principal vector) of each chromatogram against the first and second principal vectors are shown in figures 3 and 4 versus order in which the chromatograms were taken.

An analysis of these scores from the first principal component using ANOVA analysis from OMNITAB suggested that no chromatogram is significantly different from any other on a level of significance with $\alpha = 0.05$. Furthermore, one-way analysis on the scores for first principal vector (PC1) was studied by comparing the averages of the scores for chromatograms of solutions made from the same vial. Using a Scheffe pairwise multiple comparison of means [2] we found a single pair of the 9 means which were different from one another, on a level of significance with $\alpha = 0.05$. All the remaining pairs of means were not found different. The pair of vials with differing means were from the SRM 1482a grouping.

We find there is no difference between scores of the PC1 and chromatograms of SRM 1482, SRM 1482a and the division supply on a level of significance with $\alpha = 0.05$. Samples were run on four different days and we found a day to day variation in a similar analysis. This is equivalent to the day to day variation we found in the study of the match factors.

In section 3.2.1, we described a Match Factor analysis on the hexadecane peaks in the chromatograms. In this section we describe a PCA analysis on the same hexadecane peaks in the chromatograms. Any variation in these peaks would indicate chromatographic system variations and not sample to sample variations. An ANOVA study using OMNITAB made on the scores of the hexadecane peaks with its principal components was done. The scores of the principal components obtained from the

hexadecane peaks indicated that the PC1 scores for the hexadecane peaks from the same vial were no different than those from different vials on a level of significance with $\alpha = 0.05$. Moreover, the PC1 scores of hexadecane peaks associated with vials of SRM 1482, vials of SRM 1482a, and the division supply were the same on a level of significance with $\alpha = 0.05$. Using the scores with the PC1 we found that the mean scores for any day were different on a level of significance with $\alpha = 0.05$ from that of any other day. This is consistent with our finding from the match factor studies.

From the above analysis and the analysis on the match factor discussed earlier, we see almost as much variability in the hexadecane chromatograms as we see in the chromatograms from the polyethylene. Except for one pair of vials in the PCA test of SRM 1482a, the agreement among the polyethylene peaks is as good as that among the hexadecane peaks. From this we conclude that there is no statistically significant difference between the vial contents of vials labeled as SRM 1482a, SRM 1482, and the division supply.

4.0 Intrinsic Viscosity of SRM 1482a

4.1 Measurement of the Intrinsic Viscosity

Viscosity measurements were made with a Schott-Gerate Ubbelohde micro-viscometer (Schott-Gerate GMBH, Hofheim,Germany) with a Schott-Gerate constant temperature bath held at 130 °C. Flow times were measured by the Schott-Gerate AVS 400. The solvent, 1,2,4-trichlorobenzene (TCB), was obtained from Aldrich Chemical (1,2,4-trichlorobenzene, 99+ %, spectrophotometric grade, Aldrich Chemical, Milwaukee, WI) and used as received. Butylated hydroxytolulene (2,6-Di-tert-butyl-4-methylphenol), also obtained from Aldrich Chemical, was added to the solvent at about 0.7 g/L as an antioxidant.

Solution concentrations ranging from 2 g/L to 9 g/L were made directly by weight, without employing successive dilution techniques. Concentrations were calculated from densities and partial specific volumes determined earlier in this laboratory [1].

The polymer was dissolved by heating the solution to 135 °C to 140 °C in a hot air oven with occasional stirring. Solutions were then transferred to a viscometer by filtering the solution though a syringe and syringe filter heated in the same oven. The syringe filter assembly used was a Swinny Stainless 13 mm (Millipore Corp., Bedford, MA) while the filter membrane was a Millipore LSWP Mitex 5.0 μm membrane.

For each polymer concentration, flow times were measured for both solvent and solutions. Once an aliquot of solution or solvent was in the viscometer, the AVS 400 performed a number of preconditioning runs to insure that the solution or solvent comes to temperature before the actual measurements were made and recorded. The

operation of the AVS 400 took about 2 min to 2.5 min for each of the five preconditioning runs. Seven flow times were measured on each aliquot of the solvent or the solution. Flow times measured in this viscometer ranged from 45 s to 60 s.

At the beginning of an overall measurement on one solution, the viscometer was flushed with at least three solvent aliquots. Then, at least two aliquots of solvent were introduced for flow time measurements. Three aliquots of solution were used to flush the viscometer. Three aliquots of solution were then measured. Three aliquouts of solvent were used to flush the viscometer. Finally, flow time measurements were made on three aliquots of solvent.

4.2 Results

The solution viscosity $\eta(c)$ may be expanded as a power series in solution concentration

$$\eta(c) = \eta(0)\,(1+ a_1\, c+a_2\, c^2.....) \qquad (2)$$

The viscosity number is defined as

$$(\eta(c) - \eta(0))/(\,\eta(0)\, c) = a_1 + a_2\, c \qquad (3)$$

The limiting viscosity number, $[\eta]=a_1$, is the zero concentration limit of the viscosity number.

For a properly designed capillary viscometer, the solution viscosity is almost proportional to the product of the solution density and the measured flow time. The deviation from proportionality is due to a combination of kinetic energy effects and hydrodynamic effects at the end of the capillary. The manufacturer of the viscometer gives tables to correct the measured times for each of the viscometers. These corrections are designated as the Hagenbach correction. These corrections are approximately of the form $1/t_m^{\,2}$, where t_m is the measured time, and the manufacturer's corrections were fitted to that form to interpolate their correction data. This correction is applied to each average flow time for solvent or solution yielding t(c) where the c refers to the concentration of the solution being measured.

From eq. 2 then

$$K\,\rho(c)t(c)= K\,\rho(0)t(0)\,(1+ a_1\, c+a_2\, c^2.....) \qquad (4)$$

where the solvent viscosity is

$$\eta(0) = K \rho(0)t(0) \quad (5)$$

and where K is a viscometer constant.

We finally do not need to know K since we are interested in the limiting value of

$$[\eta] = (\eta(0) - \eta(0))/(\eta(0)\, c) = a_1 \quad (6)$$

Thus we may rewrite eq. 4 as

$$\rho(c)t(c) = \rho(0)t(0)\,(1 + a_1 c + a_2 c^2 \ldots) \quad (7)$$

On any given day measuring only one concentration and related solvents as described above was practical. As viscometers got dirty, they were taken out of service and similar but not identical cleaned ones used in their place. Thus the ratio, T(c), is expected to be invariant at any concentration where T(c) is

$$T(c) = (\rho(c)t(c) - \rho(0)t(0))/(\rho(0)t(0)) \quad (8)$$

Thus we fit T(c) to the expression

$$T(c) = b + a_1 c + a_2 c^2 \ldots \quad (9)$$

where we expect b=0.

The data were fit with and without assuming b=0. Except for the significant increased uncertainty in the fit when we do not force b=0 (as one expects when one increases the number of parameters fit) both a_1 and a_2 are identical within the error for the fits.

From either set of data we estimate whether there is any reason to believe that the value of the intrinsic viscosity we obtain is any different from that obtained by Wagner and Verdier [1]. Following Natrella [2] for the case of the quadratic fit with b=0, we obtain for the level of significance with $\alpha = 0.05$ an estimate of u=0.54, the upper bound to the difference allowed between the previous measured value and our current value. The value of u estimated is greater than the absolute value of the difference between the value of the intrinsic viscosity that we measured, 40.17 mL/g, and the Wagner and Verdier [1] value of 40.2 mL/g. The same holds for the fit that is not forced to zero.

From this we can assume that the value of intrinsic viscosity measured on SRM

1482a is statistically no different from that measured on SRM 1482 in 1978. Thus, the samples are expected to be the same.

For our study of uncertainty, we consider the value of *u* reported above to be the expanded uncertainty in the repeatability of the measurement. This is reported in table 2 with other contributions to the reported uncertainty of this measurement.

The coefficient a_2 is related to the Huggins constant as

$$k_h = a_2/(a_1)^2. \qquad (10)$$

From the b=0 fit we obtain the value of k_h of 0.50 g/mL . This is about 20 % to 25 % different from the value obtained by Wagner and Verdier but within a few standard deviations of their value. Since we are not certifying this value, this seems close enough to their value to make our data acceptable.

4.3 Estimating Uncertainties in the Intrinsic Viscosity Measurement

The likely sources of uncertainty are discussed in the following subsections and the tables referred to herein. For this analysis, we largely follow the paper of Wagner and Verdier [1]. The intrinsic viscosity, [η], is the limit of

$$[\eta] = \mathcal{L}\{ (\rho(c)t(c)- \rho(0)t(0))/(\rho(0)t(0))c)\} \qquad (11)$$

where $\mathcal{L}\{\}$ is taken to mean the limit at zero concentration. Following Wagner and Verdier [1] using the fact that the limit of the product is the product of the limit, they find

$$[\eta] = \rho(0)^{-1}[(1+2K/t_m(0)^{-3})/(1-K/t_m(0)^{-3}) \; X \; \mathcal{L}\{ (t_m(c)-t_m(0))/)(t_m(0))w)\}+\rho(0)^{-1}-v_{avg} \qquad (12)$$

where w is the weight fraction of solute in the solution. These are all in measurable quantities. This formula corrects a typographical error in their formula 11. The formula shows that the intrinsic viscosity as made up of two terms if we disregard the kinetic energy (KE) corrections of the viscometer. Assuming these KE corrections are zero we get then

$$[\eta] = \rho(0)^{-1} \mathcal{L}\{ (t_m(c)-t_m(0))/(t_m(0)w)\} + \rho(0)^{-1}-v_{avg} \qquad (13)$$

The last two terms are the difference between the specific volume of the solvent, $\rho(0)^{-1}$, and the specific volume of the polymer in solution, v_{avg}. This term is

small, about a few tenths of a mL/g, compared to overall intrinsic viscosities of 40 mL/g to 80 mL/g for most polymers.

4.3.1 Shear Rate Dependence of Viscosity

Low molecular weight polymers in dilute solution are expected to show little or no shear rate dependence. Wagner and Verdier [1] were unable to detect a shear rate dependence even for SRM 1484, a linear polyethylene with a M_w of 114,000 g/mol. The capillary in their viscometer was smaller than that in the Schotte-Gerate viscometer we are using. Thus, we expect no shear rate dependence of the intrinsic viscosity of SRM 1482a. We assume the uncertainty introduced in the intrinsic viscosity by disregarding this contribution is zero.

4.3.2 Solution Concentration and Density

According to Wagner and Verdier [1], their reported value of $\rho(0)$ has an estimated expanded uncertainty of 0.2 % and their reported value of v_{avg} has an expanded uncertainty of 3 % or 0.04 mL/g. We used their values $\rho(0)$ and v_{avg} in our calculations. The solvent density uncertainty leads to 0.02 % relative expanded uncertainty in intrinsic viscosity and the v_{avg} uncertainty Wagner and Verdier report leads to 0.1% relative expanded uncertainty in intrinsic viscosity. Wagner and Verdier [1] estimated an uncertainty 0.03 % in intrinsic viscosity due to the disregard of the buoyancy correction. Since we corrected for buoyancy, we take this uncertainty to be less than 0.01 % or negligible.

All solutions were prepared so that at least 60 mg SRM 1482a was used. We judge the balance used for this measurement had an expanded uncertainty of 0.1mg. We found that a consistent 0.1 mg change in the weight lead to an expanded uncertainty of 0.08 mL/g in intrinsic viscosity.

Solvents weights were measured with an expanded uncertainty of 0.01 g. A minimum of 30 g of solvent was used. This uncertainty had negligible effect on the results and so was taken to be zero.

4.3.3 Timer Uncertainties

Individual flow times were recorded to 0.01 s. We take this to be the expanded uncertainty of the timer measurements. Since the intrinsic viscosity is the ratio of the time differences over a time, only the uncertainty in the time in the denominator is important. Since total flow times were between 40 s and 60 s, a 0.01 s timer uncertainty would cause an expanded uncertainty of no more than 0.02 mL/g.

4.3.4 Kinetic Energy or Hagenbach Corrections

As noted above, kinetic energy, or Hagenbach, corrections were estimated from tables given by the viscometer manufacturer and obey a $G/t(c)^2$ law. The value of G estimated from the manufacturer's table is 412 s^3 for our viscometer. We take our value of G to have a relative expanded uncertainty of 20 %, twice that assumed by Wagner and Verdier [5] for their value of G. This leads to an expanded uncertainty of 0.04 mL/g in the intrinsic viscosity of SRM 1482a.

4.3.5 Uncertainties arising from Temperature Uncertainties

Wagner and Verdier[1] estimate the relative temperature dependence of the intrinsic viscosity of polyethylene to be no more than 0.2 %/°C for polyethylene in theta solvents. The temperature dependence is expected to less in TCB which is a good solvent for polyethylene. Following Wagner and Verdier, we take 1 %/°C as the outside limit of the temperature dependence of intrinsic viscosity. We believe the bath holds the temperature to much better than 0.3 °C including effects of temperature gradients. This conclusion arises partly because we have a reproducibility of better than 0.10 s out of about 41 s for the solvent flow time reproduced over a period of weeks. Further, we found a 1 °C change in temperature, altered the measured flow time of the solvent by 0.32 s. Thus, we take 0.12 mL/g as the expanded uncertainty from the temperature.

4.3.6 Estimated Combined Expanded Uncertainty

In table 2 the estimated expanded uncertainties from all sources are listed. Following NIST guidelines [7] we obtain the combined expanded uncertainties as the root sum of squares of these quantities.

5.0 Conclusions

The above study suggests that the bottle-to-bottle homogeneity of SRM 1482a is acceptable. Furthermore, there is no discernable difference between SRM 1482 from the SRMP shelves and SRM 1482a. Finally, the intrinsic viscosity data recently obtained on SRM 1482a matches well the intrinsic viscosity measured over 20 years ago on SRM 1482. This indicates that SRM 1482a is indistinguishable from SRM 1482

6. 0 Acknowledgments

One of us, CMG, wishes to thank Mark S. Levenson of the Statistical Analysis Division of NIST for very fruitful discussions on Principal Component Analysis and for his suggestion of it as a method to analyze the homogeneity testing of the bottling using SEC experiments.

7.0 References

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Table 1

Four Largest Eigenvalues from PCA of SRM 1482 and SRM1482a Peaks

Principal Component Number	Eigenvalue	Cumulative Percent
1	54.97	99.94
2	0.019	99.97
3	0.0086	99.97
4	0.00034	99.97

Table 2

Contributions to Expanded Uncertainty in Measured Intrinsic Viscosity of SRM 1482

Source of uncertainty	Contribution In mL/g
Shear Rate Dependence	0.0
$\rho(0)$	0.08
v_{avg}	0.04
buoyancy corrections	0.0
solute weights	0.08
solvent weights	0.0
Timer	0.02
Flow time correction factor	0.04
Measurement temperature	0.12
Uncertainty in fit of data	0.54
Combined Expanded Uncertainties in the Intrinsic Viscosity	0.57

National Institute of Standards & Technology

Certificate

Standard Reference Material® 1482a

Polyethylene

This Standard Reference Material (SRM) is intended primarily for use in calibration and performance evaluation of instruments used to determine the molar mass* and molar mass distribution by high temperature size exclusion chromatography (SEC) and instruments used to obtain the high temperature dilute solution viscosity of the polymer. A unit of SRM 1482a consists of approximately 0.4 g of polyethylene powder.

Property	Certified Value	Certified Uncertainty
mass-average molar mass, M_w, g/mol	13 600	1500
number-average molar mass, M_n, g/mol	11 400	300
intrinsic viscosity [η], mL/g	40.1	0.5

*Expressed as molar mass, previously expressed as molecular weight [1].

Certified Uncertainties: All certified measurement uncertainties are expressed as combined expanded uncertainties with a coverage factor $k = 2$, calculated in accordance with NIST procedure [5]. Type A and Type B contributions to the expanded uncertainty of the measured intrinsic viscosity include uncertainty in the fit of the data, as well as uncertainties in temperature, solvent density, solute weight, and flow time correction.

Expiration of Certification: The certification of SRM 1482a is valid, within the measurement uncertainties specified, until **26 November 2002** provided that the SRM is handled in accordance with the storage instructions given in this certificate. This certification is nullified if the SRM is modified or contaminated.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before expiration of this certificate, NIST will notify the purchaser. Return of the attached registration card will facilitate notification.

Storage: The SRM should be stored in the original bottle with the lid tightly closed under normal laboratory conditions.

Intrinsic viscosity measurements were made at 130 °C in the solvent, 1,2,4-trichlorobenzene. Butylated hydroxytoluene (2,6-di-tert-butyl-4-methylphenol) was added to the solvent at about 0.7 g/L as an antioxidant. Details of the intrinsic viscosity measurements on SRM 1482a are given in reference [2].

The support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the Standard Reference Materials Program by R.J. Gettings.

Gaithersburg, MD 20899
Certificate Issue Date: 4 December 1997

Thomas E. Gills, Chief
Standard Reference Materials Program

Homogeneity and Characterization: The homogeneity of SRM 1482a was tested by SEC analysis of solutions in 1,2,4-trichlorobenzene at 130 °C. The characterization of this polymer is described in reference [2]. SRM 1482a is a reblending and rebottling of the remaining stock of SRM 1482.

NIST Certification Method: The certified values for M_w and M_n were originally measured on SRM 1482 in 1978 [3,4] and reverified for SRM 1482a by SEC analysis. The certified intrinsic viscosity measurements were performed on SRM 1482a and compared with current measurements on control specimens of SRM 1482. There was no statistically significant difference between the values of each.

Technical measurement and data interpretation were provided by C.M. Guttman, J.R. Maurey, and W.R. Blair of the NIST Polymers Division.

The technical coordination leading to certification of this material was provided by B.M. Fanconi of the NIST Polymers Division.

Guidance concerning statistical analysis was provided by M.S. Levenson of the NIST Statistical Engineering Division.

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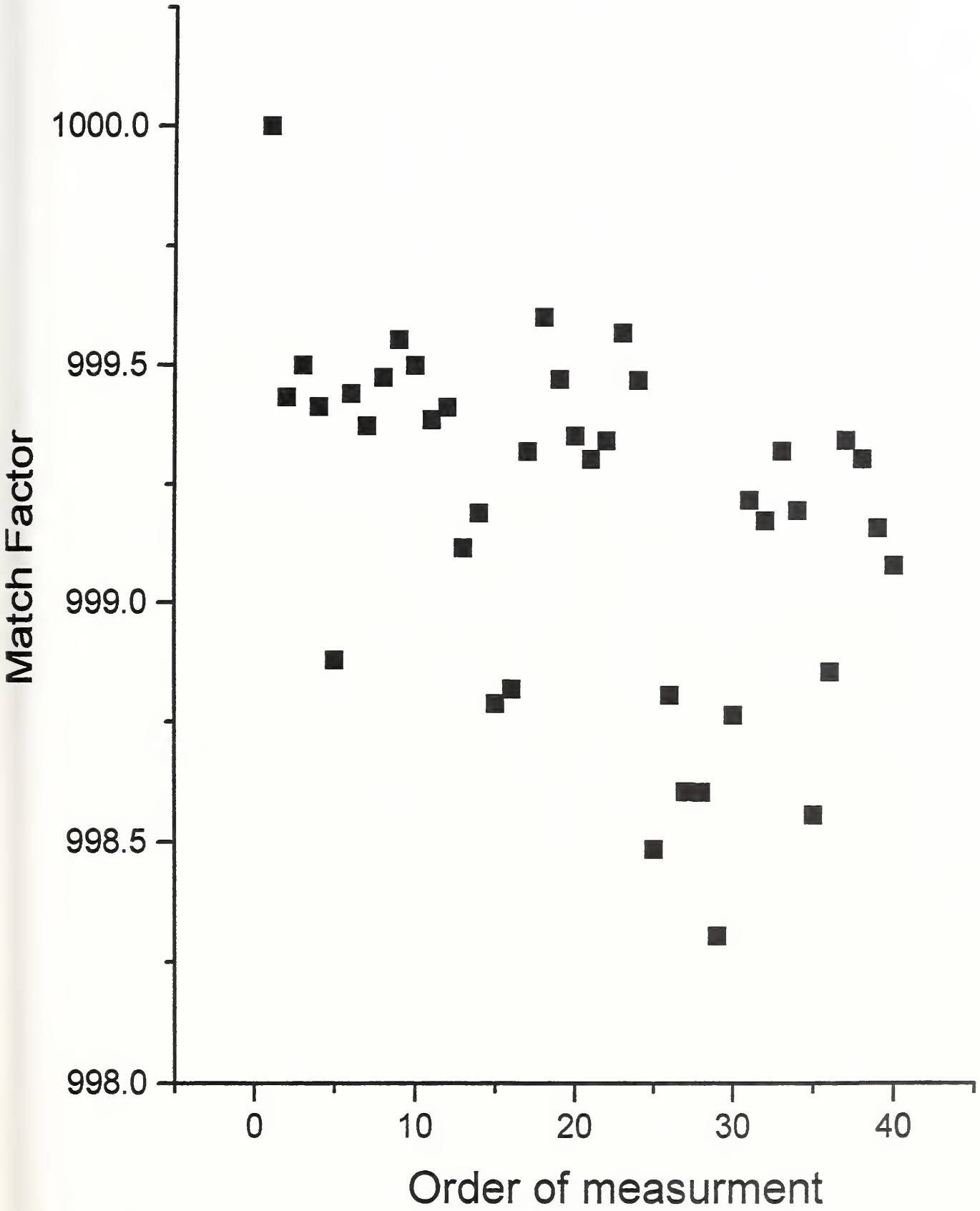
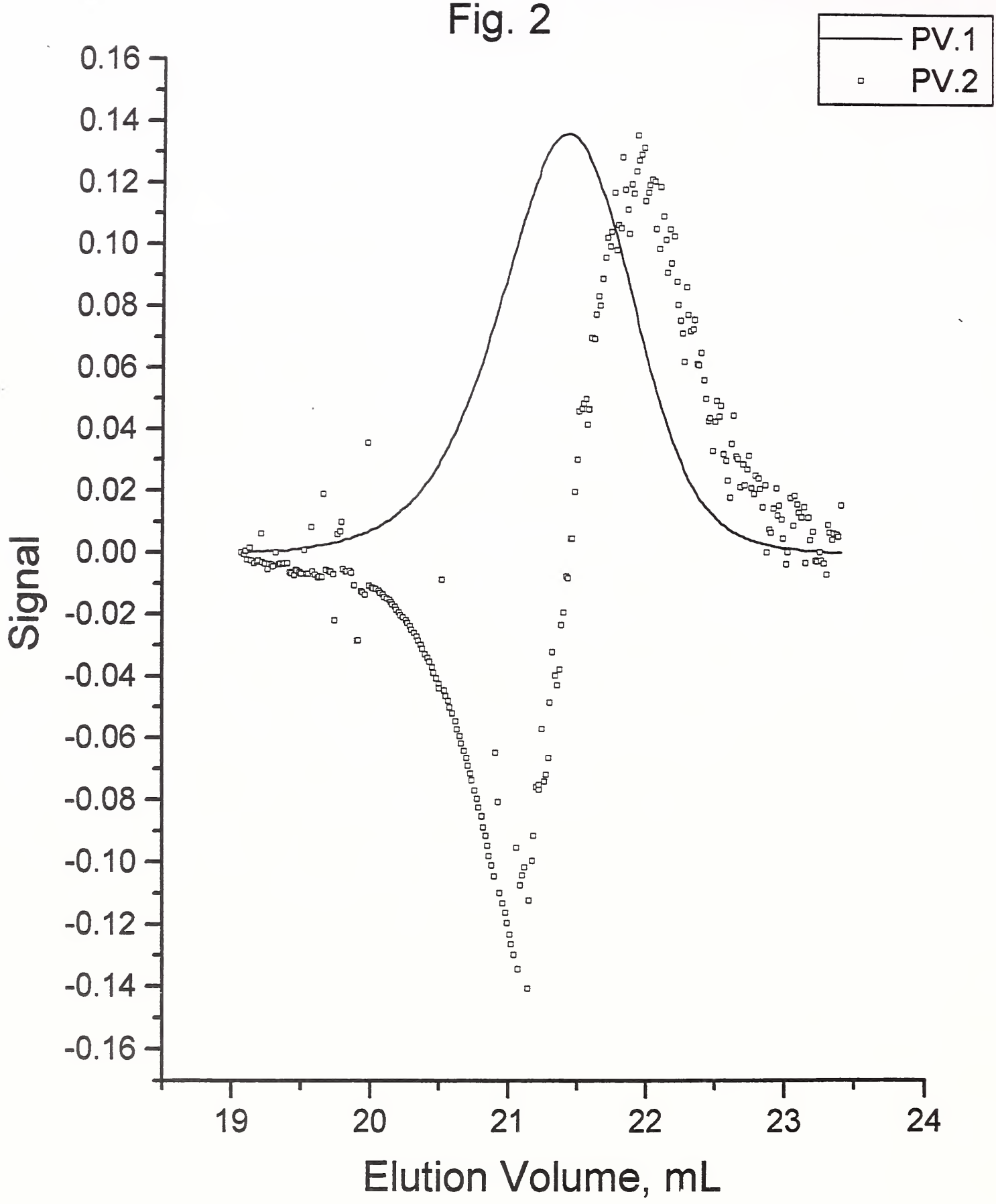
It is the responsibility of users of this SRM to assure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: Phone (301) 975-6776 (select "Certificates"), Fax (301) 926-4751, e-mail srminfo@nist.gov, or via the internet http://ts.nist.gov/srm.

Fig. 1



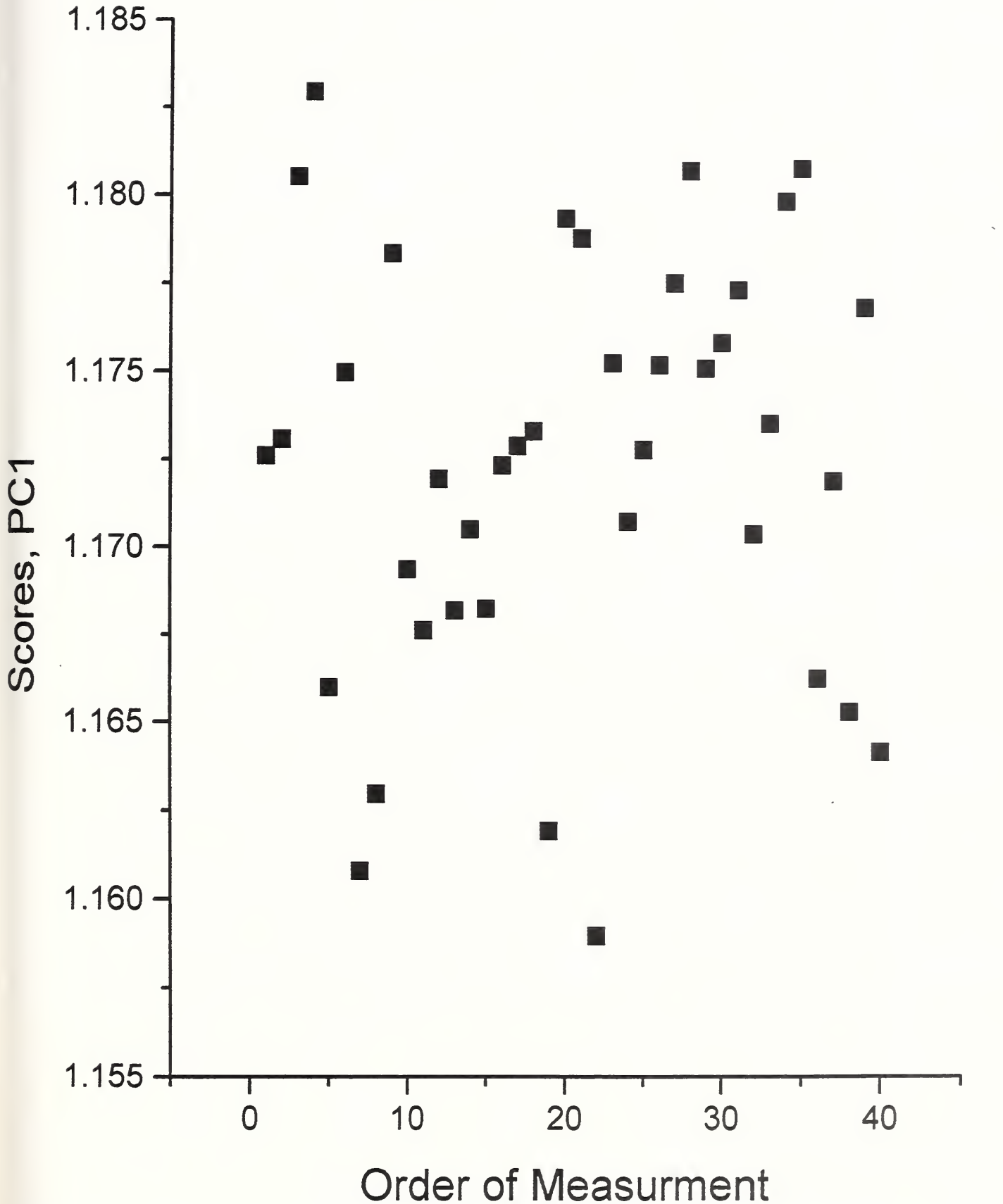
Match Factor for chromatograms for SRM 1482a,
SRM 1482 and division supply in order of measurment

Fig. 2



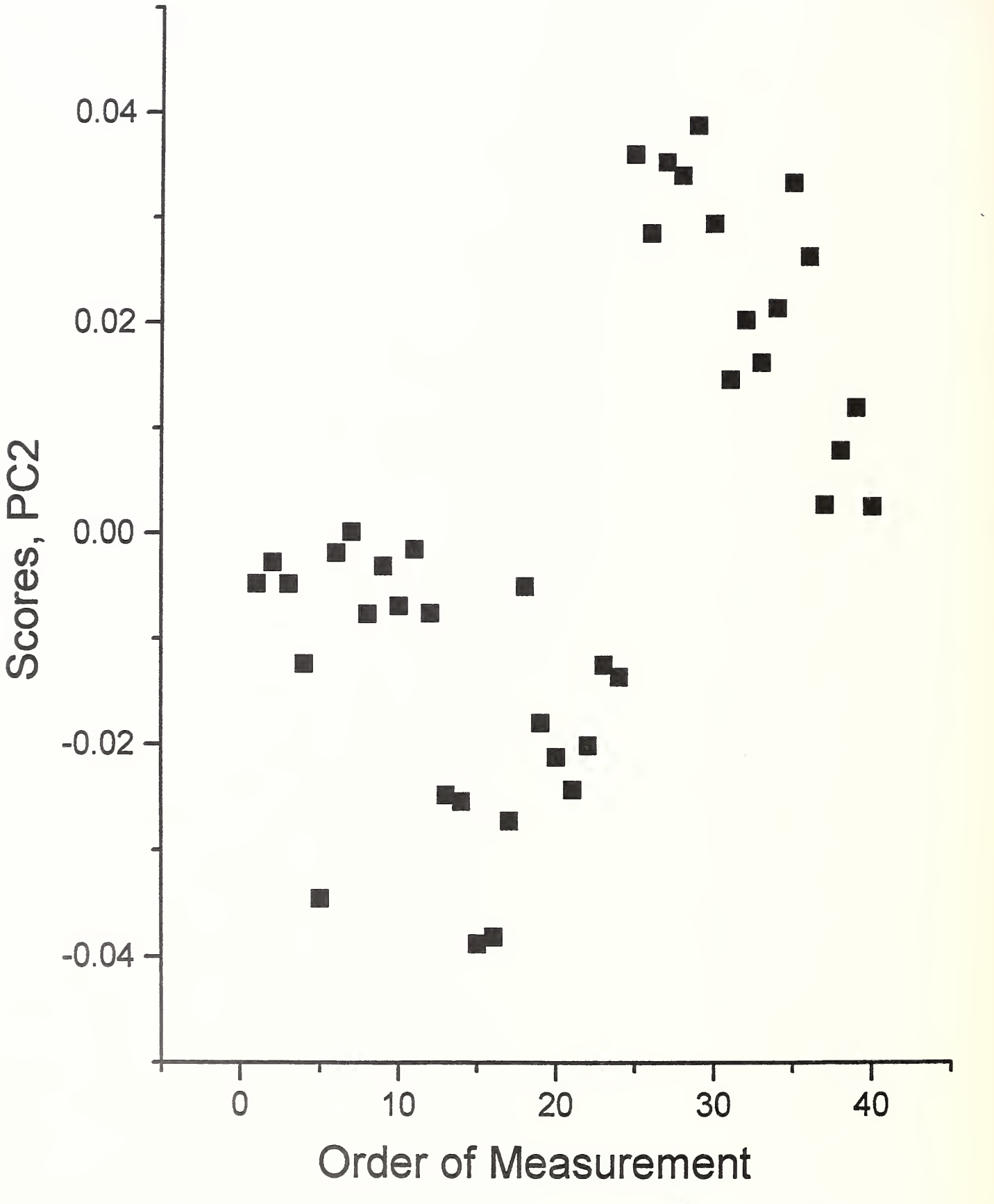
First and Second Principal Vector from SRM1482, SRM1482a and division supply chromatograms.

Fig. 4



Scores for Chromatograms from First Principal Vector

Fig. 4



Scores for Chromatograms with Second Principal Vector